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CONTINUING PATENT APPLICATION TRANSMITTAL  
(for Continuing Applications  
under 37 C.F.R. §1.53(b))

Attorney Docket No. BSCF 015 C7

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09/477470  
01/04/00

Box PATENT APPLICATION  
Commissioner of Patents and Trademarks  
ATTENTION: Assistant Commissioner  
for Patents  
Washington, D.C. 20231

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) I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" Service under 37 CFR §1.10 on the date indicated above and is addressed to the Commissioner of Patents and Trademarks, Washington, D.C. 20231.

) Julie R. Whalen

) (Typed or printed name of person mailing)

) Julie R. Whalen

) (Signature of person mailing)

Sir:

This is a request under 37 C.F.R.  
§1.53(b) for filing a:

- (X) Continuation application,  
( ) Divisional application,  
( ) Continuation-in-Part application,

Of Application Serial No. 09/140,052, filed August 26, 1998, still pending, which is a

Continuation of Serial No. 08/175,781, filed on December 30, 1993, now U.S. Patent No. 5,801,873;

Which is a Continuation of Serial No. 07/874,175, filed on April 23, 1992, now U.S. Patent No. 5,751,467;

Which is a Continuation of 07/760,877, now abandoned;

Which is a Divisional of Serial No. 07/422,601, now abandoned;

Which is a Divisional of Serial No. 06/846,354, filed March 31, 1986, now U.S. Patent No. 4,902,108.

1. (X) This is a continuation or divisional application. Enclosed is a copy of the prior application as originally filed, including specification, claims and oath or declaration. As stated in paragraph 10, new formal drawings that were submitted with the prior application are enclosed.

- or -

- ( ) Enclosed is a patent application (for continuation, divisional, or continuation-in-part applications) containing:

( ) \_\_\_\_\_ pages of the specification (including claims).

( ) \_\_\_\_\_ sheets of drawings ( ) Formal ( ) Informal.

2. (X) The entire disclosure of the prior application, from which a copy of the executed oath or declaration is supplied, is considered as being part of the disclosure of this new application under 37 C.F.R. §1.53(b), and is hereby incorporated by reference therein. A copy of the executed oath or declaration filed in the prior nonprovisional application is enclosed.

3. (X) Inventorship:

( ) A newly-executed oath or declaration and power of attorney is enclosed (for continuation-in-part applications, or for continuation or divisional applications naming an inventor not named in the prior application) (§1.63(a), (d)(5) and (e)).

(X) A copy of the executed oath or declaration and power of attorney filed in the prior nonprovisional application showing a signature, or an indication thereon that it was signed, is enclosed (for continuation or divisional applications filed by all, or by fewer than all, of the inventors named in the prior application) (§1.63(d)).

( ) Because this application is being filed by fewer than all of the inventors named in the prior application, delete the following inventor(s) named in the prior nonprovisional application (37 C.F.R. §1.63(d)(1)(2)):

\_\_\_\_\_  
\_\_\_\_\_.

( ) The names of persons believed to be the actual inventors are set forth in the enclosed unexecuted oath or declaration and power of attorney (§1.41(a) and §1.53(b)).

4. ( ) Amend the specification by inserting before the first line the sentence: --This is a [ ] continuation, [ ] division, [ ] continuation-in-part, of application number \_\_, filed \_\_\_\_\_.--

5. ( ) Assignment(s) of the invention to Gentex Corporation, and cover sheet are enclosed.

( ) A check in the amount of \$\_\_\_\_\_ to cover the fee for recording the assignment(s) is enclosed.

6. (X) The prior application is assigned of record to  
Gentex Corporation, Reel 4537, Frame 0966.

7. ( ) Small Entity Status (37 C.F.R. §1.28(a)(2)):

( ) A statement of status as a small entity is enclosed.

( ) A statement of status as a small entity was filed in the prior application, and small entity status is still proper and desired in this new nonprovisional application.

( ) Status as a small entity is no longer claimed.

8. ( ) A 37 C.F.R. §3.73(b) statement is enclosed (where an assignee seeks to take action in a matter before the Patent Office).

9. (X) A preliminary amendment is enclosed.

10. (X) Drawings:

( ) Transfer the drawings from the prior application to this application and abandon said prior application as of the filing date accorded this application. A duplicate copy of this sheet is enclosed for filing in the prior application file. (May be used only if signed by person authorized by §1.138 and before payment of base issue fee.)

(X) New formal drawings that were submitted with the prior application are enclosed.

( ) Informal drawings are enclosed.

11. ( ) A separate written request under 37 C.F.R. §1.136(a)(3), which is a general authorization to treat any concurrent or future reply requiring a petition for an extension of time under 37 C.F.R. §1.136(a) for its timely submission as incorporating a petition for an extension of time for the appropriate length of time, is enclosed.

12. (X) An Information Disclosure Statement is enclosed.

(X) A Form PTO-1449 is enclosed.

(X) 38 References (copies) listed on the Form PTO-1449 are enclosed.

13. ( ) A MicroFiche Computer Program (Appendix) is enclosed.

14. (X) A Return Receipt Postcard is enclosed (MPEP §503).

15. ( ) A Nucleotide and/or Amino Acid Sequence Submission is enclosed.

( ) A Computer Readable Copy is enclosed.

( ) A Paper Copy (Identical to Computer Copy) is enclosed.

( ) A Statement Verifying Identity of above Copies is enclosed.

16. ( ) Priority of application number \_\_\_\_/\_\_\_\_ filed on \_\_\_\_\_ in \_\_\_\_\_ is claimed under 35 U.S.C. §119.

( ) The certified copy of the priority document has been filed in prior application number \_\_\_\_/\_\_\_\_, filed \_\_\_\_\_.

( ) A certified copy of the priority document is enclosed.

( ) An English translation of the priority document is enclosed.

17. (X) Power of Attorney:

(X) The power of attorney in the prior application is to:  
Brian J. Rees Reg. No. 36,648,  
Gentex Corporation  
600 North Centennial Street  
Zeeland, Michigan 49464

( ) The power appears in the original papers in the prior application.

(X) Since the power does not appear in the original papers in the prior application, a copy of the power in the prior application is enclosed.

18. ( ) Cancel in this application original claims \_\_\_\_\_ of the prior application before calculating the filing fee. (At least one original independent claim must be retained for filing purposes.)

19. (X) The filing fee is calculated below:

Fee Calculation for Claims as Filed in the Preliminary Amendment, Less Any Claims Cancelled by Amendment

(a) Basic Fee		\$ 690.00
(b) Independent Claims	<u>6</u> - <u>3</u> = <u>3</u> x \$ 78.00 =	\$ <u>234.00</u>
(c) Total Claims	<u>16</u> - <u>20</u> = <u>0</u> x \$ 18.00 =	\$ _____
(d) Fee for Multiply Dependent Claims	\$270.00	\$ <u>270.00</u>
Total of above Calculation		\$ <u>1194.00</u>
Reduction by 50% for Filing by Small Entity		\$ _____
Total		\$ <u>1194.00</u>

20. ( ) A check in the amount of \$ \_\_\_\_\_ is enclosed.

21. (X) The Commissioner is hereby authorized to charge \$1194.00 as well as, any fees which may be required under 37 C.F.R. §§1.16 and 1.17 and are not paid herewith, or credit any overpayment, to Deposit Account Number 07-1070. A duplicate copy of this request is enclosed.

22. ( ) Also enclosed:

23. (X) Address all future communications to:

GENTEX CORPORATION  
ATTENTION: Brian J. Rees  
600 North Centennial Street  
Zeeland, Michigan 49464  
Telephone: (616) 772-1800 x365  
Facsimile: (616) 772-5223

BA  
1-4-00

(Date)

B. J. Rees

Brian J. Rees

Registration No. 36,648

(x) Attorney or agent of record

( ) Filed under §1.34(a)

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Harlan J. Byker  
Serial No. :  
Filed : Herewith  
Group Art Unit :  
Examiner :  
For : VARIABLE TRANSMITTANCE  
ELECTROCHROMIC DEVICES

**Box PATENT APPLICATION**  
**Assistant Commissioner for Patents**  
**Washington, D.C. 20231**

**EXPRESS MAIL CERTIFICATE**

**"Express Mail" Label Number : EJ551218306US**  
**Date of Deposit : January 4, 2000**

I hereby certify that the above-identified continuing patent application, attached hereto, as well as a preliminary amendment, declaration, associate power of attorney, 1.53b transmittal letter, information disclosure statement along with Form 1449 and 38 references and formal drawings are being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to Box Patent Application, Commissioner of Patents and Trademarks, Washington, D.C. 20231.

Julie R. Whalen  
Julie R. Whalen

1-04-2000  
Date

**CERTIFICATE OF MAILING (37 CFR 1.8)**

I hereby certify that I will cause this correspondence to be deposited with the U.S. Postal Service with sufficient postage as first class mail in an envelope addressed to: Assistant Commissioner for Patents, Washington, D.C. 20231, on or before January 4, 2000.

Julie R. Whalen  
Julie R. Whalen

1-04-2000  
Date

**IN THE UNITED STATES PATENT AND TRADEMARK  
OFFICE**

In re Application of : Harlan J. Byker

Examiner :

Serial No. :

Group Art Unit :

Filed : Herewith

Title: VARIABLE TRANSMITTANCE  
ELECTROCHROMIC DEVICES

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Box PATENT APPLICATION  
Assistant Commissioner for Patents  
Washington, D.C. 20231

**PRELIMINARY AMENDMENT**

Sir:

Preliminary to the examination of the continuation Application  
filed herewith, please amend as follows:

**IN THE TITLE:**

Please insert at the end of the title the following --AND  
COMPOUNDS USEFUL THEREIN--.

**IN THE SPECIFICATION:**

Prior to the first line, please insert the following:

The present application is a continuation of Application Serial No. 09/140,052, filed August 26, 1998, which is a continuation of Serial No. 08/175,781, filed on December 30, 1993, now U.S. Patent No. 5,801,873, which is a continuation of Serial No. 07/874,175, filed on April 23, 1992, now U.S. Patent No. 5,751,467; which is a continuation of 07/760,877, now abandoned; which is a divisional of Serial No. 07/422,601, now abandoned; which is a divisional of Serial No. 06/846,354, filed March 31, 1986, now U.S. Patent No. 4,902,108.

**IN THE CLAIMS:**

Please cancel claims 1-10 and insert in their place the following claims 11-23.

Claim 11. An electrochromic device, comprising a single-compartment, self-erasing, solution-phase variable transmittance component that provides continuously variable transmittance over a range of transmittance as a function of the potential difference applied, and wherein the continuously variable transmittance component comprises an acrylic material and a UV stabilizer.

Claim 12. The electrochromic device according to claim 11, wherein said acrylic material is a thickening material.

Claim 13. The electrochromic device according to claim 11, wherein said acrylic material is a gel.

Claim 14. The electrochromic device according to claim 11, wherein the sheet resistance of a transparent electrode layer of the electrochromic device is less than 40 ohms per square.

Claim 15. An electrochromic device, comprising a solution-phase, single-compartment, self-erasing variable transmittance component, where said electrochromic device is gray-scale controllable over a range of transmittance and wherein the continuously variable transmittance component comprises a gel and a UV stabilizer

Claim 16. The electrochromic device according to claim 15, where the device is gray-scale controllable by applying potential differences between electrode layers of the device of 0.2 to 1.4 volts.

Claim 17. An electrochromic device, comprising a variable transmittance component, where said electrochromic device provides continuously variable transmittance over a range of transmittance as a function of the potential difference applied, and wherein the electrochromic device comprises a UV stabilizer.

Claim 18. The electrochromic device according to claim 17, wherein the electrochromic device further comprises one of an acrylic material, a gel and a thickening material.

Claim 19. The electrochromic device according to claim 17, wherein the sheet resistance of a transparent electrode layer of the electrochromic device is less than 40 ohms per square.

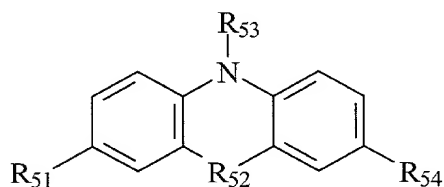


Claim 20. An electrochromic device, comprising a variable transmittance component, where said electrochromic device provides continuously variable transmittance over a range of transmittance as a function of the potential difference applied, and wherein the sheet resistance of a transparent electrode layer of the electrochromic device is less than 40 ohms per square.

Claim 21. An electrochromic device according to any of claims 11, 15, 17 and 20, wherein said device is an electrochromic window that has an area of at least about 162 square centimeters.

Claim 22. An electrochromic device, comprising a variable transmittance component, where said electrochromic device provides continuously variable transmittance over a range of transmittance as a function of the potential difference applied, where the current flow during normal device operation is 20 milliamperes per square centimeter or less, and wherein the continuously variable transmittance component comprises a gel and a UV stabilizer.

Claim 23. A compound of the formula



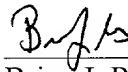
Wherein  $R_{51}$  and  $R_{54}$  are the same or different and are each selected from hydrogen and dialkylamino, wherein the alkyl groups are the same or different and each of 1 to 6 carbon atoms;  $R_{52}$  is oxygen, sulfur or  $NR_{55}$ , wherein  $R_{55}$  is the same as or different from  $R_{53}$  and both  $R_{55}$  and  $R_{53}$  are selected from hydrogen, alkyl of 1 to 10 carbon atoms,

phenyl optionally substituted at any one position with chloride, bromide, iodide, cyano, or alkyl of 1 to 4 carbon atoms, or benzyl, optionally substituted at any one position of the phenyl group with chloride, bromide, iodide, cyano, or alkyl of 1 to 4 carbon atoms.

### REMARKS

The present application contains claims 11-23. The title has been amended. It is respectfully requested that the original claims 1-10 pending be canceled and the new claims 11-23 be inserted prior to calculation of the filing fee. In view of this, it is believed that \$1194.00 is due. Please refer to the Rule 1.53(b) transmittal letter for detailed calculation of the fees due for this continuation application.

Respectfully submitted,



Brian J. Rees  
Registration No. 36,648

Gentex Corporation  
600 North Centennial Street  
Zeeland, MI 49464  
(616) 772-1800 ext. 365

January 4, 2000

SINGLE-COMPARTMENT, SELF-ERASING,  
SOLUTION-PHASE ELECTROCHROMIC DEVICES,  
SOLUTIONS FOR USE THEREIN, AND USES THEREOF

TECHNICAL FIELD

The present invention relates to devices of  
5 reversibly variable transmittance to electromagnetic  
radiation, compositions for use as media of reversibly  
variable transmittance in such devices, and use of such  
devices in variable transmission light filters and  
variable reflectance mirrors. More particularly, the  
10 invention relates to single-compartment, self-erasing,  
solution-phase electrochromic devices, solutions for use  
therein and uses thereof.

BACKGROUND OF THE INVENTION

15 Several different types of devices are known  
wherein transmittance to electromagnetic radiation can  
be reversibly varied. Among such devices are those  
wherein the transmittance is changed by thermochromic,  
photochromic, or electro-optic (e.g., liquid crystal,  
20 dipolar suspension, electrophoretic, electrochromic)  
means and wherein the variable transmittance is to  
electromagnetic radiation that is at least partly in the  
visible range (wavelength from 4200Å to 7000Å).

Devices of reversibly variable transmittance to  
25 electromagnetic radiation have found application as the  
variable transmittance element in variable transmittance  
light-filters, variable reflectance mirrors, and display  
devices which employ such light-filters or mirrors in  
conveying information. These variable transmittance  
30 light filters have included windows. The variable  
reflectance mirrors have included anti-glare rearview  
mirrors for automotive vehicles.

Devices of reversibly variable transmittance to  
electromagnetic radiation, wherein the transmittance is  
35 altered by electrochromic means, including  
electrochemichromic devices, are descibed, for example,

by Chang, "Electrochromic and Electrochemichromic Materials and Phenomena," in Non-emissive Electrooptic Displays, A. Kmetz and K. von Willisen, eds. Pergamon Press, New York, New York 1976, pp. 155-196 (1976).

5 Electrochemichromic devices includes those wherein electrochemical reactions occur in a solid film, involve electroplating or occur entirely in solution. See Chang, supra.

Numerous electrochemichromic devices are known  
10 in the art. See, e.g., Manos, U.S. Patent No. 3,451,741; Bredfeldt et al., U.S. Patent No. 4,090,782; Shattuck and Sincerbox, U.S. Patent No. 4,093,358; Clecak et al., U.S. Patent No. 4,139,276; Kissa et al., U.S. Patent No. 3,453,038; Rogers, U.S.  
15 Patent Nos. 3,652,149, 3,774,988 and 3,873,185; and Jones et al., U.S. Patent Nos. 3,282,157, 3,282,158, 3,282,160 and 3,283,656. Among these devices are single-compartment, self-erasing, solution-phase electrochromic devices. See, e.g., Manos, supra, which  
20 is incorporated herein by reference; Bredfeldt et al., supra; Shattuck and Sincerbox, supra; and Clecak et al., supra.

In a single-compartment, self-erasing, solution-phase electrochromic device, the intensity of  
25 electromagnetic radiation is modulated by passing through a solution held in the device in a compartment which includes two electrodes. The two electrodes are in contact with the solution. Between the electrodes, there is no barrier, such as a semi-permeable membrane,  
30 which would divide the solution compartment and prevent some components in the solution from diffusing or migrating from one electrode to the other. The solution includes a solvent and at least one "anodic" compound (which can be neutral or charged) and at least one  
35 "cathodic" compound (which also can be neutral or charged). The "anodic" compounds are electrochemically oxidized and the "cathodic" compounds are

electrochemically reduced when a DC electrical potential difference is impressed across the solution between the electrodes. If none of the "anodic" compounds and "cathodic" compounds to be oxidized or reduced is charged, prior to oxidation or reduction, respectively, the solution will, and otherwise the solution may, include inert, current-carrying electrolyte. The electrochemical properties of the solvent, inert, current-carrying electrolyte, if any, anodic compounds, cathodic compounds, and any other components that might be present in the solution are preferably such that the anodic and cathodic compounds are oxidized and reduced, respectively, at a potential difference between the electrodes which does not cause any significant electrochemical or other changes in the other components in the solution. The solution is fluid during operation of the device, although it may be gelled or made highly viscous with a thickening agent. That the devices are "solution-phase" means that all of the components in the solution, including the anodic and cathodic compounds, remain in solution during operation of the device with the concomitant oxidation of anodic compounds and reduction of cathodic compounds.

Reversible modulation of intensity of electromagnetic radiation passing through a single-compartment, self-erasing, solution-phase electrochromic device can be accomplished because of three factors related to operation of the device. First, the molar extinction coefficients of the anodic compounds and cathodic compounds in the solution of the device, as a function of wavelength, change with their electrochemical oxidation and reduction, respectively. Generally, at least one of these compounds undergoes a significant change in extinction coefficient at wavelengths in the visible range upon the oxidation or reduction; consequently, the solution and device change color or change from dark to clear or clear to dark when

a potential difference is applied across the solution between the electrodes. Second, in the solution, the oxidized anodic compounds and reduced cathodic compounds do not, to any significant extent, undergo degradative reactions unimolecularly or with other components.

5 Third, in the solution, the oxidized anodic compounds react substantially only with the reduced cathodic compounds to yield substantially only anodic compounds and cathodic compounds in their forms and with their properties prior to the oxidations and reductions,

10 respectively. These reactions of oxidized anodic compounds with reduced cathodic compounds provide the "self-erasing" feature to the device.

Heretofore, no single-compartment, self-erasing, solution-phase electrochromic devices have

15 been known which have proven to be suitable for commercial application as the component of reversibly variable transmittance in variable transmittance light filters or variable reflectance mirrors. For such applications, the solution of variable transmittance

20 must be highly stable to cycling, at least several thousands of times, from zero potential difference between the electrodes to a potential difference between the electrodes that is sufficient to cause significant change in transmittance and then back to zero again. In

25 a typical device, the solution is held in a layer between planar, parallel, spaced-apart, transparent walls, on the inside surfaces of which (in contact with the solution) are coated thin layers of transparent, electrically conductive material which serve as

30 electrodes and through which passes electromagnetic radiation whose intensity is reversibly modulated in the device. It is advantageous to have the solution layer as thin as possible, in order to minimize distortion of light passing through, or passing into and reflecting

35 out of, a device, and to reduce to durations that are acceptable for commercial applications the "response

time" required for the transmittance of a device to achieve a new steady-state value when the potential difference between the electrodes is changed. However, for devices with thin solution layers, anodic and  
5 cathodic electrochromic compounds must be found that, at concentrations in the solution at which they remain soluble, both at zero-potential equilibrium and when oxidized (in the case of anodic compounds) and reduced (in the case of cathodic compounds) when a potential  
10 difference is applied between the electrodes, give rise to sufficiently large changes in absorbance between their zero-potential equilibrium states and their "activated" (i.e., oxidized or reduced) states and at the same time remain sufficiently stable to cycling to  
15 provide a commercially practicable device. The present invention addresses the need for solutions to make commercially practicable single-compartment, self-erasing, solution-phase electrochromic devices.

A useful feature in such devices, that has not  
20 heretofore been available, is the capability to function as a gray-scale device, i.e., to vary continuously and rapidly in transmittance to light in the visible wavelength range as a function of the potential difference applied between the electrodes of the  
25 device. Such a "gray-scale" device would find application in a window, which would allow light of constant intensity to pass through independently of the intensity of the light reaching the window, and an anti-glare rearview mirror in an automobile, that would  
30 reflect light of acceptable intensity to the driver regardless of the intensity of the glare-causing light incident on the mirror from headlamps of automobiles approaching the vehicle from behind. The present invention provides gray-scaling capability in  
35 single-compartment, self-erasing, solution-phase electrochromic devices.

A problem that has not heretofore been recognized with solution-phase electrochromic devices is segregation, due to both migration and natural convection of anodic and cathodic electrochromic compounds. Particularly in devices that are operated continuously for long periods (more than about 20 minutes) with the planar surface through which light enters the device oriented vertically to the ground, such segregation can cause annoying and troublesome separation of color and reduction in speed of self-erasing. The present invention addresses this segregation problem.

Variable reflectance mirrors include a variable transmittance component, which is a device which has a transmittance to visible light which is reversibly varied by thermochromic, photochromic, or electro-optic means, and a reflection means, which is a highly reflective surface (such as a silver layer) from which light is reflected after passing through a medium of reversibly variable transmittance in the variable transmittance component. After reflecting from the reflection means, the reflected light passes back through the medium of reversibly variable transmittance. The medium of variable transmittance in such mirrors is typically held, in the variable transmittance component, between two planar, parallel, spaced-apart surfaces. At least one of these surfaces is transparent to light, and light reflected by the mirror enters and leaves through this transparent surface. A problem with such mirrors is the high "residual" reflectivity, which is usually greater than 5%, of this transparent surface of the variable transmittance component. For example, in an anti-glare rearview mirror for an automobile, wherein elimination of high glare may require reduction of reflectivity observed by the driver from all surfaces to as low as about 5 to 7%, the high residual reflectivity of the



front surface of a typical mirror requires that the transmittance of the medium of reversibly variable transmittance in the mirror be capable of being made as low as about 3%. Because it is difficult to achieve  
5 such low transmittance with sufficient speed in preferably thin devices of reversibly variable transmittance, it would be advantageous to have variable reflectance mirrors wherein these problems caused by high residual reflectivity are avoided. The present  
10 invention provides such mirrors.

#### SUMMARY OF THE INVENTION

The present invention provides solutions for use as the medium of reversibly variable transmittance  
15 to electromagnetic radiation, particularly light in the visible range, in single-compartment, self-erasing, solution-phase electrochromic devices.

The invention provides further such electrochromic devices, wherein a solution of the  
20 invention is the medium of reversibly variable transmittance; variable transmission light filters and variable reflectance mirrors, wherein the variable transmittance component is a single-compartment, self-erasing, solution-phase device according to the  
25 invention; and display devices wherein information is displayed by operation of variable transmission light filters or variable reflectance mirrors according to the invention.

The solutions of the invention render  
30 commercially practical the use of single-compartment, self-erasing, solution-phase electrochromic devices and variable transmission light filters, variable reflectance mirrors and display devices employing such filters and mirrors. The solutions of the invention are  
35 unexpectedly highly stable to cycling of potential differences between the electrodes in devices of the invention.

In devices of the invention wherein the solution layer is desirably thin, and with concentrations of anodic and cathodic compounds in the solution that are low enough that precipitation does not occur and problems of segregation are substantially  
5 reduced, and at potential differences between the electrodes that are low enough to avoid significant degradation of the solution, the solutions of the invention darken to an unexpectedly high absorbance to visible light with unexpectedly high speed once the  
10 potential difference is applied and clear again with unexpectedly high speed once the electrodes are open-circuited or short-circuited. Advantageously, reversal of the polarity of the electrodes of a device of the invention is not required for clearing to occur  
15 with sufficient speed for many practical applications. Further, devices of the invention can advantageously be operated as gray-scale devices.

In another aspect, the present invention entails novel electrochromic compounds and combinations  
20 of compounds for use in solutions of the invention.

In still another aspect, the invention includes an improved variable reflectance mirror, wherein variable reflectance is provided by thermochromic, photochromic, or electro-optic means in a device of  
25 variable transmittance to electromagnetic radiation. In such an improved mirror of the invention, problems due to residual reflectivity from a planar surface through which light enters, and after reflecting from the reflecting means, leaves the mirror are avoided by  
30 displacing this planar surface at a slight angle to the highly reflective planar surface of the mirror which is its reflecting means. Thereby, a person viewing the mirror need not see light due to residual reflectivity simultaneously with light that is reflected from the  
35 mirror's reflecting means.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 displays schematically an exploded view of two planar, transparent, electrode-bearing sides, 100 and 130, of a device of the invention together with spacer or separating means, 11, which holds the electrode-bearing sides apart and substantially parallel in an assembled device of the invention and the inside edges, 11A, 11B, 11C and 11D of which, together with the electrode layers, 10A and 13A, of the electrode-bearing sides, defines a space, 12, which, in an assembled device of the invention, is occupied by a solution according to the invention that is in contact with the electrode layers.

FIGURE 2 illustrates schematically a partially assembled device, 200, according to the invention. FIGURE 2 shows, by cross-hatched area 14, the portion, of planar, transparent side 100 of the device, which overlays the solution of reversibly variable transmittance in the device and which, consequently, changes color, or changes from clear to dark and back, as the device is operated.

FIGURE 3 illustrates schematically a view of a cross-section of a partially assembled, improved variable reflectance mirror, 300, according to the invention, wherein the reflecting means is the highly reflective layer 18A of a prism-shaped mirror, 180, laminated to surface 131 of one transparent, electrode-bearing side, 130, of a variable transmittance device according to the invention.

FIGURE 4 illustrates schematically a view of a cross-section of a partially assembled, improved variable reflectance mirror, 400, according to the invention, wherein the reflecting means is a high reflectance layer, 20, on one electrode-bearing side, 130, of a variable transmittance device according to the invention and a transparent prism-shaped object, 22, is laminated to the surface 101 of the other

electrode-bearing side, 100, of the variable transmittance device according to the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

5 In one of its aspects, the present invention is a solution, for use as the variable transmittance medium in a single-compartment, self-erasing, solution-phase electrochromic device, which comprises:

(A) a solvent;

10 (B) at least one cathodic electrochromic compound which, in a voltammogram done <sup>with an inert electrode</sup> in the solvent at <sup>room temperature</sup>, displays at least two chemically reversible reduction waves, with the first of said reductions accompanied by an increase in molar extinction coefficient at at least one wavelength in the visible range;

H.J.Z.  
3-29-86

15 (C) at least one anodic electrochromic compound which, in a voltammogram done <sup>with an inert electrode</sup> in the solvent at <sup>room temperature</sup>, displays at least two chemically reversible oxidation waves, with the first of said oxidations accompanied by an increase in molar extinction coefficient at at least one wavelength in the visible range; and

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20 (D) if all cathodic and anodic compounds in their zero-potential equilibrium states in the solution are not ionic, an inert current-carrying electrolyte.

The solutions of the invention are optionally gelled or thickened by being combined with an agent, such as acrylic sheet material, derived, for example, from LUCITE L<sup>R</sup>.

30

In another of its aspects, the instant invention is a single-compartment, self-erasing, solution-phase electrochromic device which comprises, as the medium of reversibly variable transmittance to light, a solution of the invention. The solution of reversibly variable transmittance in a device of the invention is optionally gelled or thickened.

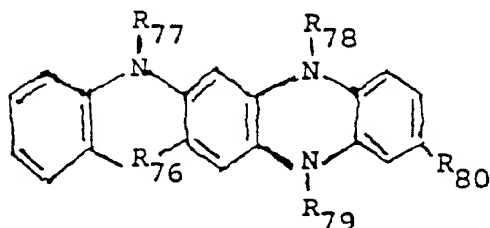
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In another aspect, the present invention entails a variable transmittance light-filter which comprises, as the variable transmittance element, a single-compartment, self-erasing, solution-phase device of the invention.

In a further aspect, the invention entails a variable reflectance mirror which comprises, as the variable transmittance element, a single-compartment, self-erasing, solution-phase device of the invention.

In a still further aspect, the invention includes a display device which comprises, as an information-conveying element, a variable transmittance light filter or variable reflectance mirror according to the invention.

In another aspect, the invention includes a compound of Formula LII



LII

wherein R<sub>76</sub> is oxygen or sulfur, R<sub>80</sub> is hydrogen or dialkylamino, wherein the alkyl groups are the same or different and are each of 1 to 6 carbon atoms, and R<sub>77</sub>, R<sub>78</sub> and R<sub>79</sub> are the same or different and are each selected from hydrogen, alkyl of 1 to 6 carbon atoms, phenyl optionally substituted at any one position with an alkyl group of 1 to 6 carbon atoms, and benzyl, optionally substituted at any one position of the phenyl group with an alkyl group of 1 to 6 carbon atoms.

In still another aspect, the present invention includes a variable reflectance mirror which comprises a device of reversibly variable transmittance, a planar front surface, and a planar reflecting means,

(A) said device comprising

(i) a medium of transmittance which is reversibly varied by thermochromic, photochromic, or electro-optic means, and

5 (ii) two planar, parallel, spaced-apart surfaces, between which the medium of reversibly variable transmittance is held and through which light passes prior to and after reflecting from said reflecting means; with

10 (B) the angle between the plane of said front surface and the plane of said reflecting means being about  $1^{\circ}$  to about  $5^{\circ}$ .

In the mirrors, a significant improvement arises from the positioning of the plane of the reflecting means at a slight angle to the plane of the front surface of the mirror, i.e., the surface through which light reflected by the mirror from the reflecting means enters and leaves the mirror. This positioning of these planes permits the mirror to be oriented so that light from outside the mirror that is reflected from the front surface of the mirror without entering the mirror (i.e., light from residual reflectivity of the front surface) is not seen by the person using the mirror while light reflected from the reflecting means is seen by such person. Thus, to reduce reflection (including reflected glare) from such a mirror, the residual reflectivity of the front surface of the mirror does not need to be overcome and, consequently, the extent to which the medium of reversibly variable transmittance needs to be darkened is reduced in comparison with the darkening that would be required if the reflecting means were parallel to the front surface. Further, various distortions in reflected images that occur, when both light reflected due to residual reflectivity of the front surface of a mirror and light reflected from the reflecting means of the mirror are observed, are avoided when only light from the reflecting means is seen.

15  
20  
25  
30  
35

Although any medium whose transmittance to visible light can be reversibly altered by thermochromic, photochromic, or electro-optic means can be employed as the medium of reversibly variable transmittance in these improved mirrors of the invention, it is most preferred that the medium be a solution according to the present invention (optionally gelled or thickened) and that the device of reversibly variable transmittance be a single-compartment, self-erasing, solution-phase device according to the present invention, which has two planar, parallel, spaced-apart sides, at least one of which is transparent (and through which light reflected by the mirror from the reflecting means passes prior to and after reflecting from the reflecting means) and the other of which, if not transparent, has a highly reflecting layer, which serves as the reflecting means of the mirror, adhered to its side opposite the side in contact with the solution.

Construction and operation of single-compartment, self-erasing, solution-phase electrochromic devices, essentially the same as those of the present invention but having different solutions of reversibly variable transmittance, are known in the art. See Manos, Bredfeldt et al., Shattuck and Sincerbox, and Clecak et al., supra.

In Figure 1, the basic structural elements of a typical device of the invention are illustrated in an exploded view. These elements include two planar electrode-bearing sides or walls, 100 and 130, a spacing or separating layer, 11, which spaces apart and holds parallel the walls 100 and 130 in an assembled device, and surrounds a space or volume, 12. Volume 12 is defined, in an assembled device, by electrode layers, 10A and 13A, of the electrode-bearing walls 100 and 130, respectively, as well as the four inside walls, 11A, 11B, 11C and 11D, of layer 11 (In Figure 1, inside

walls 11B and 11C are hidden from view.)). In an assembled device, volume 12 is filled (or nearly filled, in case room is left for expansion with temperature increase) with a solution according to the invention, which has reversibly variable transmittance in operation of the device. The solution in volume 12 is in contact with both electrode layers 10A and 13A during operation of the device.

Usually, and preferably, in an assembled device, walls 100 and 130, including electrode layers 10A and 13A, and the layers 10 and 13, respectively, of the solid material to which the electrode layers adhere, are planar and parallel. By "planar" and "parallel" in the present specification are meant planar and parallel, respectively, within normal tolerance limits, as understood in the art, taking account of possible slight variations arising from slight deviation in uniformity of thickness at different points (e.g., of each of layers 11, 10, 10A, 13 and 13A in the Figures), flexibility of materials, and the like.

However, it is to be understood that, as long as volume 12 can be sealed after being filled (or nearly filled) with solution, electrode-bearing layers 100 and 130 can be other than planar and can be spaced so that their inner, electrode layers are other than equidistant at each point (provided the electrode layers do not come into contact with each other). Further, although in the preferred devices layer 100 and layer 130 will be made from the same materials, having electrode layers (10A, 13A) of the same thickness and same material, having solid material layers (10, 13) of the same thickness and same material, and otherwise be essentially the same, it is not necessary that this be the case. The electrode layers, like the solid material layers, can be of different materials and different thicknesses.

In typical devices of the invention, solid material layers, 10 and 13, of walls 100 and 130,



respectively, will be made of clear glass or clear plastic, between 0.05 cm and 1 cm thick, which are suitable for coating with layers of electrically conducting material, to form electrode layers 10A and 13A. Layers 10 and 13 can, however, be made of any material which is transparent and to which an electrically conducting material can be affixed to form electrode layers.

Electrode layers, 10A and 13A, can be made of any electrically conducting material that can be adhered in a layer to the material of solid material layers, 10 and 13, respectively, and that is essentially chemically inert to the solutions of reversibly variable transmittance that are employed in devices of the invention. Suitable materials for the electrode layers are thin, transparent layers of gold, tin oxide, ruthenium oxide, cadmium stannate, and indium-doped tin oxide ("ITO"), or thin, highly reflective layers of materials such as rhodium, or Inconel. Preferred is ITO. Methods of applying the electrically conducting material to the solid material, of layers 10 and 13, to form suitable electrode layers are known in the art. Preferably, as illustrated in Figures 1 and 2, the electrode layer will cover the entire surface of a solid material layer, over the volume 12 and spacer 11 as well as on an extension of the solid material layer beyond an outside wall of spacer 11 (i.e., with reference to Figure 1, a wall of spacer 11 opposite wall 11A, 11B, 11C or 11D). The electrode layer will preferably have a thickness that is as uniform as possible over the entire surface of the solid material layer to which it is affixed; the thickness of the electrode layer will preferably be such that it has a resistivity of less than 100 ohms per square and, more preferably, less than 40 ohms per square. It is, however, not necessary that the electrode layer cover the entire solution volume of a device of the invention or extend outside the spacer

which holds apart electrode-bearing walls of the device, as long as electrical contact can be made with the layer and, in operating the device, solution in the solution space is in contact with the electrode layer. Further,  
5 it is not required that the electrode layer have uniform thickness or that it have a resistivity less than 100 ohms per square.

It is also possible, in a device of the invention, to have one or both electrodes separate from  
10 solid material layers, such as 10 and 13 in the Figures. With reference to Figure 1, in place of electrode layers 10A and 13A, electrode strips could, for example, be situated along and parallel to sides 11B and 11D. Alternatively, one of electrode layers 10A and  
15 13A could be replaced with an electrode plate or strip parallel to but not adhered to solid material layer 10 or 13, respectively. If the electrodes are separate from the solid material layers, the electrodes as well as the solid material layers are of material that is  
20 essentially chemically inert to solutions of the invention. In such devices, glass is a suitable material for the solid material layers and rhodium or platinum are suitable as electrodes.

The devices of the invention reversibly  
25 modulate the intensity of light that enters and leaves the device. Thus, in a device of the invention, at least part of at least one wall of the solution space is transparent to light of a range of wavelengths which includes at least a part of the range of wavelengths  
30 over which the transmittance of the solution of the invention in the solution space is reversibly varied in operation of the device. In the typical device, the entire area of both walls of the solution space will be transparent to light of all wavelengths in at least the  
35 visible range.

In a preferred variable transmittance light filter according to the invention, the device of

reversibly variable transmittance will be a device according to the invention wherein both walls of the solution space (e.g., 100 and 130 in Figure 1) are transparent to visible light of all wavelengths.

5           To prepare a variable reflectance mirror according to the invention, a highly reflecting layer, such as of silver, can be applied to the outside (i.e., the side opposite the solution) of one of the transparent walls of the solution volume of a device  
10 according to the invention, wherein, but for the reflecting layer, both walls of the solution space would be transparent. Alternatively, a variable reflectance mirror can be made by employing for one of the electrode layers defining the solution space in a device, a highly  
15 reflecting, electrically conductive material such as rhodium or Inconel.

As described further below, transparent walls of a device of the invention, defining the solution volume, can be joined, bonded or laminated to plates of  
20 glass or plastic, mirrors, and the like to make variable transmittance light filters and variable reflectance mirrors according to the invention wherein variable transmittance to light is provided by a device of the invention.

25           In the present specification, "transparent" to light of a range of wavelengths means that at least some light, of all wavelengths in the range, passes through, instead of being absorbed or reflected. Use of the word "transparent" without qualification means transparency  
30 to light of a range of wavelengths which includes at least all wavelengths in the visible range (wavelength from 4200 Å to 7000 Å). Typically, and as a practical matter, a transparent wall of the solution volume of a device of the invention will allow at least about 90% of  
35 the light, at all wavelengths in the visible range, that is incident on it to pass through, rather than be reflected or absorbed.

In contrast, a "highly reflecting" surface, within the meaning of the present specification, is one that reflects, rather than transmits or absorbs, at least about 50%, and more typically at least about 70%, of light of all wavelengths in an identified range. If used without qualification, a surface that is "highly reflecting" is one that is so to light of all wavelengths at least in the visible range.

The spacer, denoted as 11 in the Figures, is electrically insulating and is made of a combination of a sealing material, such as epoxy resin, silicones, rubber cement, low melting glass, certain plastics, parafin wax, or the like, with a spacing material such as small glass beads, nylon monofilament, MYLAR<sup>R</sup> strips, polystyrene beads or the like. As indicated above, the spacer is preferably of substantially uniform thickness so that the two walls defining the solution space in a device can be held essentially parallel to each other. Although shown schematically as planar in Figure 1, the inside edges 11A, 11B, 11C and 11D of the spacer, and the outside edges opposite the inside edges, are in reality curved or rough edged. This curvature or roughness will be clear from the manner by which a typical device is assembled: by placing strips of a (highly viscous) mixture, of sealing material with spacing material, around an area on the inside (i.e., electrode layer bearing side) of one wall of a device and then pressing the other wall of the device, with its inside (i.e., electrode-bearing side) wall facing the inside of the first wall, against the strips until both walls contact the separating means. This pressing squeezes excess sealing material in the strips from the strips and causes the outside and inside edges of the strips to be curved or uneven. In the devices of the invention, the separating material in the spacer holds the inside (i.e., electrode-bearing) surfaces of walls between about 0.0025 to about 0.05 cm apart. A

preferred spacer is a combination of glass beads with epoxy resin sealant.

The electrodes of a device of the invention are connected to, or capable of being connected to, a  
5 DC power source, whereby an electrical potential can be impressed between the electrodes and across the solution in a device. In the device illustrated schematically in Figure 2, a preferred arrangement for connecting the electrodes to a power source is illustrated. In this  
10 arrangement, the two electrode-bearing walls are displaced in opposite directions, laterally from but parallel to the solution space, in order to provide an exposed strip of each of the electrode surfaces. To each of these exposed strips is adhered, so as to be in  
15 electrical contact with the strip along nearly its entire exposed length, an electrically conductive strip or wire, such as a copper, aluminium or silver strip or wire. One such strip, 16, is shown in its entirety in Figure 2 and in cross-section in Figures 3 and 4. Only  
20 the lead or extension, 15A, of the other strip 15 of the device of Figure 2 is seen in Figure 2. Strip 15 is seen in cross-section in Figures 3 and 4. Like strip 16 affixed to electrode-layer 13A, strip 15 is affixed to electrode layer 10A along essentially the entire length  
25 of the overhang of the electrode layer. Although any means known in the art can be employed to secure the wire or strip in electrical contact with the electrode surface, such as clamping, soldering or securing with a conductive adhesive, a preferred means is to use a  
30 conductive epoxy, such as standard silver epoxy. The strips or wires affixed to the electrode surfaces have leads or extensions, illustrated by 15A and 16A in Figure 2 beyond the ends of the electrode surfaces. Connection to a suitable power source is effected by  
35 standard electrical connection from the power source to these leads or extensions.

Assembly of a device of the invention can be carried out as understood in the art. See Manos, supra. A preferred method for assembling a device is as follows:

5           A strip of spacer material, consisting of a separating material, such as glass beads, mixed with a sealing material, such as insulating epoxy, is deposited on one surface of the device (on the electrode surface thereof, in the preferred case wherein the surface of  
10 the device is a planar piece of solid material, such as glass, to which is affixed or adhered a layer of electrically conducting material to serve as an electrode) to outline a cross-sectional area, of desired size and shape, for the solution volume. The solution  
15 volume is then formed by placing the other surface of the device over the strip of spacer material, so that the electrode layers of the surfaces face each other, and then applying pressure to the two surfaces to cause them to approach each other until they are separated  
20 substantially only by the separating material in the spacer. If the solution used with the device is to be thickened by combination with a thickener, such as acrylic sheet material, as derived from LUCITE L<sup>R</sup>, a solution of the thickener in a volatile solvent such as  
25 dichloroethane, acetone or methyl ethylketone is conveniently painted or sprayed on the entire area outlined by the spacer on the first wall, and the solvent allowed to evaporate, prior to application of the second wall. After the assembly process, and prior  
30 to filling with a solution, the sealing material of the spacer is allowed to cure, if necessary, to become inert to the solution; such curing is necessary when the solvent of the solution is propylene carbonate and the sealing material is insulating epoxy.

35           The shape of the solution volume, viewed in cross-section through the electrode-bearing walls, is not constrained to be square or rectangular. It can be

circular, elliptical, polygonal, in the shape of a letter or numeral, or any desired shape.

One of the walls of a device of the invention has bored therein (prior to assembly) two small holes  
5 located, in the assembled device, over and near the edge of, the solution volume (e.g., with reference to Figure 1, one near inside wall 11A and the other near inside wall 11B). The device is filled with solution of the invention through these holes by passing solution in  
10 through one of them while allowing air to escape out the other. After the filling, the two holes are sealed first with a conventional thermoplastic material inert to the solution and secondarily with a sealant such as, for example, insulating epoxy.

15 Then conducting wires or strips, usually copper strips, are adhered, usually with a conducting epoxy such as a standard silver epoxy, to the exposed portions of both electrode surfaces. Finally, employing the sealing material used in the spacer, the wires or  
20 strips, except for the leads or projections thereof through which contact with a power source is made, are sealed over, as is the entire periphery of the device, i.e., the outside of the rim or sides which include the spacer.

25 For solvent in a solution of the invention, any compound, or mixture of compounds, can be employed, which is liquid over the range of temperatures, at which the solution of the invention is to be used as the medium of reversibly variable transmittance in a device  
30 of the invention, and which is known to be useful as a solvent in the electrochemical arts. As a practical matter, for convenience in preparing the solutions and because devices of the invention usually will be operated over a range of temperatures which includes  
35 room temperature, a solvent will be liquid over at least the range between 20°C and 27°C (i.e., room temperature). Further, it is preferred, for the sake of

stability of devices of the invention, that the solvent of solution of the invention not undergo electrolysis or be involved in other, irreversible chemical reactions, during storage or normal operation of a device.

- 5 Suitable as solvents are water, methanol, ethanol, acetonitrile, N,N-dimethylformamide, dimethylsulfoxide, acetone, methyl ethyl ketone, cyclopentanone, and cyclic esters, including propylene carbonate, ethylene carbonate,  $\beta$ -propiolactone,  $\beta$ -butyrolactone, 10 gamma-butyrolactone, gamma-valerolactone, delta-valerolactone or homogeneous (i.e., single-phase) mixtures of them. It is preferred that the solvents be substantially free of dissolved oxygen and, but for water, be anhydrous. Preferred solvents are the cyclic 15 esters or combinations thereof. Most preferred is propylene carbonate.

In a solution of the invention, there is at least one cathodic electrochromic compound, at a concentration at 25°C of at least  $10^{-4}$  M up to its 20 solubility, but more usually between about 0.01 M and 0.1 M, which, in the solvent of the solution, as determined by standard voltammetric techniques <sup>at an inert electrode</sup> at room temperature, has at least two chemically reversible (i.e., ~~quasi-reversible~~ <sup>H.G.P. 3-29-86</sup> but not necessarily kinetically 25 reversible, as understood in the electrochemical arts) reduction waves, the first of these reductions being accompanied by an increase in the extinction coefficient of the cathodic compound at at least one wavelength in the visible range.

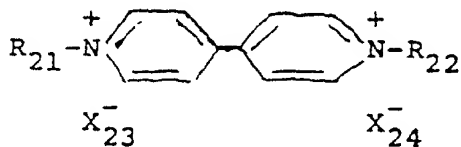
30 Further, in a solution of the invention, there is at least one anodic electrochromic compound, at a concentration at 25°C of at least  $10^{-4}$  M up to its solubility, but more usually between about 0.01 M and 0.1 M, which, in the solvent of the solution, as 35 determined by standard voltammetric techniques <sup>at an inert electrode</sup> at room temperature, has at least two chemically reversible (as understood in the electrochemical arts) oxidation <sup>H.G.P. 3-2</sup>



waves, the first of these oxidations being accompanied by an increase in the extinction coefficient of the anodic compound at at least one wavelength in the visible range.

5 Usually it is intended that, upon application of a potential difference across the solution between the electrodes of a device of the invention, the solution change from clear to dark or change color. Thus, it is desirable that the first chemically  
10 reversible reduction of a cathodic electrochromic compound or first chemically reversible oxidation of an anodic electrochromic compound employed in a solution of the invention be accompanied by an increase in extinction coefficient, in the solvent of the solution  
15 at room temperature, of a factor of at least about  $10^2$  to at least about  $10^3 \text{ cm}^{-1} \text{ M}^{-1}$  at at least one wavelength in the visible range.

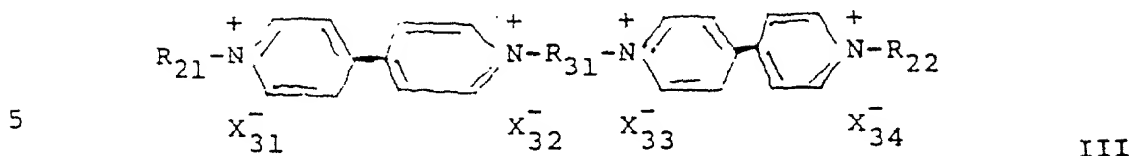
Among the cathodic electrochromic compounds suitable for solutions of the invention are the known  
20 compounds of Formula II (viologens)



II

wherein  $\text{R}_{21}$  and  $\text{R}_{22}$  are the same or different and are each selected from alkyl of 1 to 10 carbon atoms, phenyl optionally substituted at any one position with  
30 chloride, bromide, iodide, cyano, or an alkyl group of 1 to 4 carbon atoms, and benzyl, wherein the phenyl group is optionally substituted at any one position with chloride, bromide, iodide, cyano, or an alkyl group of 1 to 4 carbon atoms; and wherein  $\text{X}_{23}^-$  and  $\text{X}_{24}^-$  are  
35 the same or different and are each selected from chloride, bromide, iodide,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{ClO}_4^-$

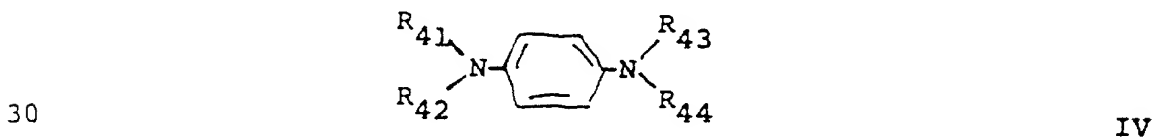
and  $\text{NO}_3^-$ ; and the known compounds of Formula III



wherein  $R_{21}$  and  $R_{22}$  are the same or different and are defined as above for the compound of Formula II,  
 10  $R_{31}$  is alkylene of 1 to 10 carbon atoms, and  $X_{31}^-$ ,  $X_{32}^-$ ,  $X_{33}^-$  and  $X_{34}^-$  are the same or different and each selected from chloride, bromide, iodide,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{ClO}_4^-$  and  $\text{NO}_3^-$ .

The preferred compounds of Formulas II and III  
 15 are those wherein all of the anions are the same and are  $\text{ClO}_4^-$  or  $\text{BF}_4^-$ . Most preferred is  $\text{BF}_4^-$ . The preferred cations of compounds of Formula II are those wherein  $R_{21}$  and  $R_{22}$  are the same and are benzyl, phenyl or n-heptyl; most preferred is benzyl. The most  
 20 preferred cation of compounds of Formula III is that wherein  $R_{31}$  is  $-(\text{CH}_2)_4-$  and  $R_{21}$  and  $R_{22}$  are the same and are benzyl (i.e., tetramethylene bis[4(1-benzyl-pyridine-4'-yl)pyridinium]).

Among the anodic electrochromic compounds  
 25 suitable for solutions of the invention are the known compounds of Formula IV

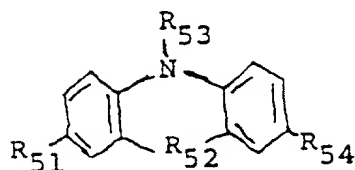


wherein  $R_{41}$ ,  $R_{42}$ ,  $R_{43}$  and  $R_{44}$  are the same or different and are each selected from hydrogen, alkyl of 1 to 10 carbon atoms, phenyl optionally substituted at  
 35 any one position with chloride, bromide, iodide, cyano, or an alkyl group of 1 to 4 carbon atoms, and benzyl, wherein the phenyl moiety is optionally substituted at

any one position with chloride, bromide, iodide, cyano,  
or an alkyl group of 1 to 4 carbon atoms;

the known compounds of Formula V

5

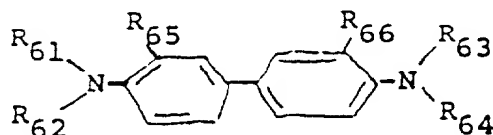


V

wherein R<sub>51</sub> and R<sub>54</sub> are the same or different and  
10 are each selected from hydrogen and dialkylamino,  
wherein the alkyl groups are the same or different and  
are each of 1 to 6 carbon atoms; R<sub>52</sub> is oxygen, sulfur  
or NR<sub>55</sub>, wherein R<sub>55</sub> is the same as or different  
15 from R<sub>53</sub> and both R<sub>55</sub> and R<sub>53</sub> are selected from  
hydrogen, alkyl of 1 to 10 carbon atoms, phenyl  
optionally substituted at any one position with  
chloride, bromide, iodide, cyano, or alkyl of 1 to  
4 carbon atoms, or benzyl, optionally substituted at any  
one position of the phenyl group with chloride, bromide,  
20 iodide, cyano, or alkyl of 1 to 4 carbon atoms;

the known compounds of Formula VI

25



VI

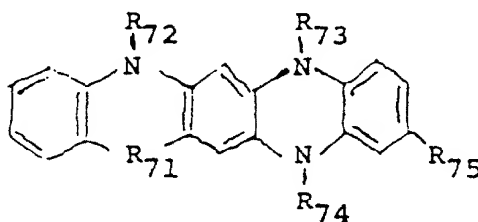
wherein R<sub>61</sub>, R<sub>62</sub>, R<sub>63</sub> and R<sub>64</sub> are the same or  
different and are each selected from alkyl of 1 to  
10 carbon atoms or phenyl; and R<sub>65</sub> and R<sub>66</sub> are the  
30 same or different and are each selected from hydrogen or  
alkyl of 1 to 10 carbon atoms, provided that both R<sub>65</sub>  
and R<sub>66</sub> are hydrogen or both are alkyl, and if R<sub>65</sub>  
and R<sub>66</sub> are both hydrogen, not more than one of R<sub>61</sub>  
and R<sub>62</sub> is hydrogen and not more than one of R<sub>63</sub> and  
35 R<sub>64</sub> is hydrogen;

the known compound of Formula VIII  
(tetrathiafulvalene)



VIII.

Also suitable as an anodic compound in  
solutions of the invention is a novel compound of the  
invention, of Formula VII



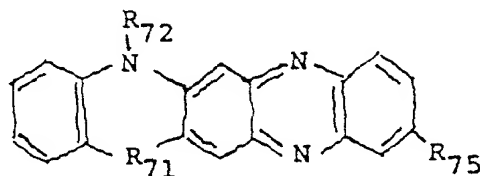
VII

wherein  $R_{71}$  is oxygen or sulfur,  $R_{75}$  is hydrogen or  
dialkylamino, wherein the alkyl groups are the same or  
different and are each selected from alkyl of 1 to  
6 carbon atoms, and  $R_{72}$ ,  $R_{73}$  and  $R_{74}$  are the same  
or different and are each selected from hydrogen, alkyl  
of 1 to 6 carbon atoms, phenyl, optionally substituted  
at any one position with an alkyl group of 1 to 6 carbon  
atoms, and benzyl, optionally substituted at any one  
position of the phenyl group with an alkyl group of 1 to  
6 carbon atoms.

Most preferred among the compounds of  
Formula VII is that wherein  $R_{71}$  is oxygen,  $R_{75}$  is  
hydrogen and  $R_{72}$ ,  $R_{73}$  and  $R_{74}$  are all methyl.

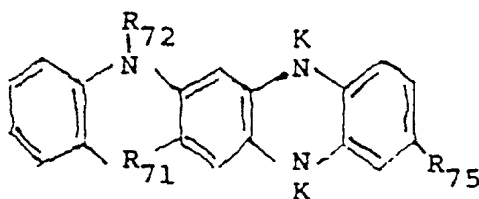
Preferred among the anodic electrochromic  
compounds for solutions of the invention are those of  
Formulas IV and V. More preferred are those of  
Formula IV wherein  $R_{41}$ ,  $R_{42}$ ,  $R_{43}$  and  $R_{44}$  are the  
same and are methyl or phenyl, and those of Formula V  
wherein  $R_{51}$  and  $R_{54}$  are hydrogen,  $R_{52}$  is the same  
as  $N-R_{53}$  and  $R_{53}$  is methyl or phenyl. Most  
preferred are N,N,N',N'-tetramethyl-1,4-phenylene  
diamine and 5,10-dihydro-5,10-dimethylphenazine.

Preparation of the novel compounds of the invention, of Formula VII, follows known procedures of Gilman and Dietrick (J. Amer. Chem. Soc. 79, 6178 (1957)), beginning with the known compound of Formula XX



XX

wherein R<sub>71</sub>, R<sub>72</sub> and R<sub>73</sub> are as defined above for compounds of Formula VII, to form the potassium adduct of Formula XXI



XXI

and then reacting the adduct with a mixture of compounds of Formula R<sub>73</sub>I and R<sub>74</sub>I where R<sub>73</sub> and R<sub>74</sub> are as defined above for the compound of Formula VII and can be the same, to yield the desired product after crystallization. This synthetic procedure is illustrated in Example XI, with the synthesis of the preferred N,N',N"-trimethyltriphenazinoxazine.

A solution of the invention will include inert, current-carrying electrolyte, if none of the cathodic electrochromic compounds and anodic electrochromic compounds, in their zero-potential equilibrium states in the solution, is ionic, and otherwise may optionally include such inert, current-carrying electrolyte. The inert, current-carrying electrolyte will, during normal operation of a device of the invention, carry current across the solution between the electrodes and, during

storage or normal operation of a device, will not undergo electrolysis or other irreversible chemical reactions with other substances in the device so as to impair the stability of the device.

5           The inert, current-carrying electrolyte in a solution of the invention will consist of any combination of substances known in the art to be suitable for inert, current-carrying electrolyte (sometimes referred to in the art as "supporting  
10 electrolyte"). Such substances include alkali metal salts, tetraalkylammonium salts, and aluminium chloride and bromide. Preferred as cations in inert, current-carrying electrolyte in solutions of the invention are lithium, sodium, and tetraalkylammonium,  
15 wherein the alkyl groups are the same; most preferred is tetra-n-butylammonium. Preferred as anions in inert, current-carrying electrolytes in solutions of the invention are chloride,  $\text{BF}_4^-$  and  $\text{ClO}_4^-$ ; most preferred in  $\text{BF}_4^-$ . The concentration of inert,  
20 current-carrying electrolyte, if present in the solution of the invention, will be between 0.005 M to 2 M at 25°C. More preferably, it will be between 0.05 M and 0.5 M at 25°C.

          The solutions of the invention are for use as  
25 the variable transmittance medium in a single-compartment, self-erasing, solution-phase electrochromic device. Because the devices are "solution-phase", the concentrations of substances in the solution, for a device to be operated over a given  
30 temperature range with the potential applied across the solution not exceeding a given maximum, must be such that precipitation of substances from the solution does not occur, both at zero-potential equilibrium and during operation of a device, when cathodic electrochromic  
35 material(s) is (are) being reduced at the cathode and anodic electrochromic material(s) is (are) being oxidized at the anode. Generally, provided that, at

zero-potential equilibrium at all temperatures in the range of intended use, all substances are present in the solution at concentrations below their solubilities, precipitation will not occur during operation of a  
5 device which includes the solution as the medium of reversibly variable transmittance.

The "self-erasing" property of devices of the invention means that, after a potential difference between the electrodes of a device is decreased or  
10 eliminated, the transmittance of the solution in the device will increase spontaneously, without need for reversal of the polarity of the electrodes, to a value characteristic of the new potential difference. The  
"self-erasing" feature of the devices of the present  
15 invention is provided by the spontaneous, apparently diffusion-limited, reactions of oxidized anodic compounds with reduced cathodic compounds to yield anodic compounds and cathodic compounds in their respective zero-potential equilibrium states.

20 It is important, in practical applications of the devices of the invention, that both decrease in transmittance of the solution of a device, that occurs when the potential difference between the electrodes is increased, and the increase in transmittance of the  
25 solution of a device, that occurs with self-erasing, occur sufficiently rapidly. It is generally advantageous that both decrease and increase in transmittance occur as rapidly as possible. Until the instant invention, cathodic and anodic compounds meeting  
30 the voltammographic and colorimetric criteria specified above, were not combined in a solution. It has not been realized in the art that, by having both cathodic and the anodic compounds in a single-compartment, solution-phase electrochromic device that undergo  
35 increases in absorbance in the wavelength range of interest, with reduction and oxidation, respectively, that the speed of transmittance decrease could be a

speed acceptable for commercial application of such devices without causing commercial application-defeating loss in the speed of transmittance increase, by self-erasing, made possible by the solution-phase  
5 characteristic of the devices.

Further, for practical applications of devices of the invention, it is important that the solutions in the devices be stable, both during periods when the device is not being operated and during cycling  
10 (i.e., when the potential between the electrodes of a device is cycled between zero or a low value to a higher value and back and, as a result, the transmittance of the solution in the device varies reversibly between higher and lower values). Lack of stability is  
15 indicated by an increase in absorbance of white light, or light of wavelengths at which absorbance is varied with the device, passing through the device, including the solution therein, when the solution is at zero-potential equilibrium, i.e., equilibrium with no  
20 potential difference between the electrodes of the device.

A problem preventing commercial application of single-compartment, self-erasing, solution-phase electrochromic devices has been the lack of stability of  
25 the solutions of variable transmittance employed with them. While the reasons for this instability of prior art devices are not entirely clear, they might be related to the chemical instability, and high reactivity, with solvent and other materials, of either  
30 or both of the anodic and cathodic compounds, in their oxidized and reduced states, respectively, that have been used in prior art solutions. The present invention has solved this problem with discovery that, with cathodic and anodic electrochromic compounds satisfying  
35 the above-specified voltammographic criteria, a property of the solutions of the invention is exceedingly and unexpectedly high stability, particularly stability to cycling.



It has been found that the stability of the solutions of the invention is further enhanced by minimizing in the solutions the concentration of oxygen and, if the solvent is non-aqueous, water. Thus, 5 optionally but preferably, a device of the invention is flushed with dry nitrogen or other inert gas prior to being filled with solution. Standard techniques are employed to reduce the concentrations of oxygen and, if solvent is non-aqueous, water, in solvent and solutes 10 used to prepare solutions and to minimize contamination of solutions with oxygen and water prior to filling the devices with the solutions and sealing the filled devices. For example, dry nitrogen can be bubbled through solutions prior to filling to reduce oxygen 15 concentration. Solvent can be treated by passing over a dessicant, such as activated alumina, to reduce water contamination, prior to being used to prepare a solution. In addition, solutes (electrochromic compounds; inert, current-carrying electrolyte) can be 20 dried prior to use to prepare solutions by heating to about 110°C. Alternatively, prepared solutions can be passed through a dessicant, such as activated alumina, prior to filling a device with them.

Other than any of the aforementioned measures, 25 that might be taken to reduce the concentrations of oxygen and water in solutions of the invention, solutions of the invention are prepared by standard methods, usually at room temperature, by simply dissolving the appropriate amounts of solutes in the 30 solvent to achieve the desired concentrations.

Certain advantages are realized by employing thickened or gelled solutions as the media of reversibly variable transmittance in devices of the invention. As described supra and further below, it has been 35 discovered in connection with the present invention that segregation is a problem with single-compartment, self-erasing, solution-phase electrochromic devices when

they are operated continuously for long periods.  
Gelling or thickening the solutions of the invention  
reduces the significance of the segregation problem by  
reducing the component of the segregation that is due to  
5 natural convection.

Another advantage realized by using gelled or  
thickened solutions in the devices of the invention  
relates to convenience and safety. If a device should  
be opened, as by breaking one of the transparent sides  
10 or otherwise, a gelled or thickened solution would flow  
much more slowly than a non-gelled or non-thickened one  
and, consequently, the ease of cleaning up the solution  
would be increased and the risk of persons' contacting  
any noxious or harmful substances that might be present  
15 in the solution would be reduced. In devices, wherein  
the transparent sides or other elements might shatter or  
splinter during breakage, a gelled or thickened solution  
would tend to hold the broken pieces in place and  
thereby reduce the risk of injury that might occur if  
20 the device broke apart.

The terms "thicken" and "gel" are used  
interchangeably in the instant specification and refer  
to the increase in viscosity of a solution that results  
from combining it with certain substances, whether or  
25 not a true gel is formed in the process. Any substance  
which can thicken a solution, without reacting to form  
covalent bonds with solvent, inert, current-carrying  
electrolyte or anodic or cathodic compounds therein, can  
be employed to thicken or gel a solution of the  
30 invention. The desired amount of thickening or gelling  
substance can simply be combined with solution, just  
prior to filling a device, provided there is sufficient  
time for such filling prior to the solution's becoming  
too viscous. Alternatively, the desired amount of  
35 thickening or gelling substance can be placed into a  
device before or after introduction of solution and the  
mixture with solution be accomplished in situ in the

solution space of the device; an example of this method, in which the thickener is introduced before the solution, is provided in Example X.

The concentration of thickening or gelling substance employed to prepare a thickened or gelled solution of the invention will vary, depending on a number of factors, as understood by the skilled. These factors include the thickening or gelling substance employed, the solvent employed and the desired viscosity of the thickened or gelled solution. With the preferred solvent, propylene carbonate, and the preferred thickener for this solvent, the composition obtained by dissolving the acrylic sheet material sold under the trademark LUCITE L, in an organic solvent such as acetone, methyl ethyl ketone or dichloroethane, the concentration of thickener in solution will be between about 3% (w/w) and about 30% (w/w), preferably between about 5% (w/w) to about 25% (w/w), and most preferably between about 7% (w/w) and about 15% (w/w).

Manos, supra, lists certain other thickeners which can be employed to make thickened or gelled solutions of the invention. It has been found in connection with this invention, with propylene carbonate solvent, that the composition, obtained by dissolving the acrylic sheet material sold under the trademark PLEXIGLAS in an organic solvent such as acetone, methyl ethyl ketone, or dichloroethane, can also be used for the thickening.

The preferred thickener is obtained by mixing a solvent, such as dichloroethane (1,2-dichloroethane, 1,1-dichloroethane or mixtures of the 1,1 and 1,2 isomers) with the commercially available acrylic sheet material, LUCITE L<sup>R</sup>, separating the resulting solution from any residue, and, finally, allowing the solvent to evaporate. The residue left after the solvent evaporates is the "acrylic sheet material thickener."

It has been discovered unexpectedly, in connection with the instant invention, that using this preferred thickener is unusually convenient and exceptionally suitable for constructing devices of the invention which employ propylene carbonate solutions as media of reversibly variable transmittance. This convenience and suitability is due to the facts, illustrated in Example X, that a quantity of thickener can be placed in a device by simply painting or spraying the solution of the thickener on the electrode-bearing side of a wall of the device and then allowing the solvent to evaporate before assembling the device and that the thickener inside the device is spontaneously taken up by and thickens a propylene carbonate solution of the invention, after the assembled device is filled with the solution in the usual manner.

An unexpected and highly desirable property, discovered in connection with the instant invention, of solutions of the invention thickened with the preferred acrylic sheet material thickener is that the time required for coloring of a device wherein such a solution is employed as the medium of reversibly variable transmittance is not significantly increased over the time required for coloring in a device which is the same but for having no thickener in the solution. Thus, with such thickener, the aforementioned advantages of using a thickened solution as the medium of reversibly variable transmittance in a device of the invention can be realized without significant effect on the advantage, of rapid coloring, of devices which employ non-thickened solutions of the invention as media of reversibly variable transmittance.

To be operated, a device of the invention is connected to a power source capable of establishing a potential difference of constant polarity between the electrodes of the device. Referring to Figures 1 and 2, this connection is effected through leads 15A and 16A of

the electrically conducting wires or strips affixed to the electrode layers of the walls of the device so as to be in electrically conductive contact with the electrode layers. The power source can be any AC or DC power source known in the art; however, if an AC source, control elements, such as diodes, are placed between the power source and the electrodes of the device to insure that the potential difference between the electrodes does not change in polarity with variations in polarity of the potential from the source. Suitable DC power sources are storage batteries, such as automobile batteries and dry cell batteries. The power from the power source delivered to the electrodes of the device is controlled by any means known in the art so that the potential across the solution between the electrodes of the device does not exceed the potential difference at which irreversible reactions, such as electrolysis of solvent, reduction or oxidation of inert, current-carrying electrolyte, unimolecular degradation reactions of electrochromic compounds and the like, occur. Preferably, to make use of the gray-scaling capability of the devices of the invention, the control of power delivered to the electrodes of the device will be such that the potential can be varied, over a range from about 0.1 volt to a potential somewhat below that at which irreversible reactions occur to a significant extent in the device, but held constant at any desired potential in this range. There will also be a switching means associated with the power source so that the potential between the electrodes of the device can be reduced to zero, by open-circuiting or short-circuiting. Because, in certain instances, the additional speed in self-erasing that can be achieved by applying a potential for a brief period (e.g., about 0.5 to about 5 seconds) to the electrodes, with polarity reversed from that during decreasing transmittance, the switch means may also include means for accomplishing

such reversals. The means for controlling the potential delivered to the electrodes and the switching means can be either manually or automatically operated.

In order for the electrochromic compounds in  
5 the solutions of the invention to be oxidized and reduced, and thereby cause decrease in transmittance of the solution, the potential difference between the electrodes must be high enough to cause a current to flow across the solution between the electrodes. A  
10 potential difference between about 0.3 volts and about 0.5 volts is usually adequate to cause current to flow and solution of the invention to begin to darken or change color.

The extent of darkening at steady state in a  
15 particular device of the invention will depend on the potential difference between the electrodes; because of this property the devices of the invention are useful as "gray-scale" devices.

The maximum potential that can be applied  
20 between the electrodes of a device without impairing the stability of the solution will, as the skilled understand, depend on a number of factors, such as the potential at which electrolysis of solvent occurs and potentials at which degradative reactions of  
25 electrochromic compounds occur. Devices of the invention wherein water is solvent in the solution will generally be operated at less than about 1.4 volts to avoid electrolysis of water. The devices of the present invention with cyclic ether solvents can, in some cases,  
30 be operated at a potential difference as high as about 4 volts across the solution layer. Generally, however, the potential across the solution layer in devices of the invention is kept below 2 volts.

The skilled will understand that, at steady  
35 state at a given potential across the solution layer of a device of the invention, cathodic electrochromic compounds are being reduced and anodic electrochromic

compounds are being oxidized continuously at the electrodes while, at the same time and at the same rate at which electrochemical oxidation and reduction are occurring, reduced cathodic compounds are being oxidized back, and oxidized anodic compounds reduced back, to their zero-potential equilibrium forms by reaction of reduced cathodic with oxidized anodic compounds. The rate at which the steady-state is achieved, at a given potential across the solution of a device, is dependent on the current across the solution at the potential. This current is generally not regarded as an independent variable in operation of the devices, as it depends on other factors which are independently varied, such as the conductivity of the solution in the device (which in turn depends on solution composition, including composition of inert, current-carrying electrolyte), and the potential across the solution. However, the currents that flow during normal device operation are typically in the range of 0.1 to 20 milliamperes per square centimeter of cathode or anode area in contact with solution layer.

As indicated, supra, a problem that has been discovered in connection with the present invention is that segregation occurs in single-compartment, self-erasing, solution-phase electrochromic devices that are operated continuously (i.e., held at non-zero potential) for long periods, longer than about 20 minutes. This segregation appears to be similar to the segregation that is encountered in operation of large scale electrochemical cells. Thus, the segregation found in devices of the instant invention has a component due to migration of charged electrochromic compounds in electrical potential gradients in the solution layer of a device and a component due to natural convection, which arises from different local densities, one higher and one lower than bulk solution density, around oxidized anodic and reduced cathodic molecules.

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In its final aspect, the instant invention relates to improved variable reflectance mirrors, preferred embodiments of which are illustrated schematically, in cross-sectional views, in mirrors 300 and 400 of Figures 3 and 4, respectively. As described, supra, the improvement in these mirrors arises from the positioning of the planar reflecting means, shown as 18A in Figure 3 and 20 in Figure 4, at a slight angle to the planar front surface of the mirror, which is shown as surface 101 of solid material layer 10 of wall 100 of mirror 300 in Figure 3 and surface 221 of prism-shaped piece 22 of mirror 400 in Figure 4. The front surface of the mirror is the surface through which light passes to enter and leave the mirror.

These mirrors of the invention comprise a device of reversibly variable transmittance through which light passes before and after reflecting from the reflecting means.

The device of reversibly variable transmittance is characterized by two planar, parallel, spaced-apart surfaces which are transparent to light of at least the wavelengths at which reflectance of the mirror is varied, and preferably to light of all wavelengths in at least the visible range, and between which is located a medium of absorbance which is reversibly variable by thermochromic, photochromic or electro-optic means in operation of the device. With reference to mirror 300 illustrated in Figure 3 and mirror 400 illustrated in Figure 4, these surfaces are surface 101 of solid material layer 10 and surface 131 of solid material layer 13.

Although, in mirrors 300 and 400 of Figures 3 and 4, respectively, the devices of reversibly variable transmittance, with surfaces 101 and 131, are electrochromic devices that are substantially the same as the device of the present invention illustrated in Figure 2, the improved mirrors of the invention are not

limited to having single-compartment, self-erasing, solution-phase electrochromic devices according to the instant invention as the device of reversibly variable transmittance. Any device of transmittance varied by  
5 thermochromic, photochromic or electro-optic means can be employed to vary the reflectance of an improved mirror of the invention, provided that the medium of variable transmittance is held in such device between two planar, parallel, spaced-apart surfaces which are  
10 transparent to light of at least the wavelengths at which the reflectance of the mirror is to be varied. A number of types electro-optic devices, suitable for this purpose, are known (e.g., liquid crystal devices, dipolar suspension devices, electrophoretic devices,  
15 two-compartment electrochemichromic devices such as described by Kissa, supra).

In one type of improved, variable reflectance mirror according to the invention, which is illustrated by mirror 300 of Figure 3, a prism-shaped mirror, 180,  
20 is laminated through a transparent laminating material, indicated by layer 19, to a surface, 131, of the device of reversibly variable transmittance. The prism-shaped mirror could be, for example, a conventional, prism-shaped mirror employed in rearview mirrors of  
25 automobiles. The prism-shaped mirror consists essentially of a prism-shaped piece, 18, of transparent solid material, such as of glass or a clear plastic, and a layer, 18A, of highly reflective material, such as silver, adhered to a surface of the solid material by  
30 any standard technique in the mirror-fabricating art so that a high fraction, preferably at least about 80%, of the light passing through the solid material and reaching the reflective material layer is reflected back through the solid material. The highly reflective  
35 surface of the prism-shaped mirror covers at least the entire cross-sectional area, illustrated by 14 in Figure 2 but not shown in the cross-sectional view of

Figure 3, of reversibly variable transmittance of the device of reversibly variable transmittance of the improved mirror. Highly reflective layer 18A is the reflecting means of the improved mirror of the invention.

5 In another type of improved variable reflectance mirror according to the invention, similar to that illustrated in Figure 3, the layer of laminating material is not present. Instead, the surface of the prism-shaped mirror which is not coated with a highly  
10 reflective layer is coated with an electrically conducting layer, to function as an electrode of the device of reversibly variable transmittance, and the prism-shaped mirror, with electrode layer, replaces wall 130 as one wall of said device.

15 In still another type of improved, variable reflectance mirror according to the invention, which is illustrated by mirror 400 of Figure 4, the reflecting means is a layer, 20, of highly reflective material, such as silver, adhered, by any standard technique in  
20 the mirror-fabricating art, to surface 131 of the device of reversibly variable transmittance so that a high fraction, preferably at least about 70%, of the light passing through the device of reversibly variable transmittance that reaches the reflective material is  
25 reflected back through surface 131. Further, in the type of improved mirror illustrated by mirror 400 of Figure 4, the surface, illustrated by 101, of the device of reversibly variable transmittance, that is parallel to and spaced-apart from surface 131, is laminated  
30 through a transparent laminating material, indicated by layer 21, to a prism-shaped piece, 2, of transparent solid material, such as glass or clear plastic, one surface, 221, of which is the front surface of the improved mirror through which light reflected by  
35 reflecting means 20 enters and leaves the mirror. The highly reflecting layer 20 and prism-shaped piece 22 cover at least the entire cross-sectional area,

illustrated by 14 in Figure 2 but not shown in the cross-sectional view of Figure 4, of reversibly variable transmittance of the device of reversibly variable transmittance of the improved mirror.

5 In yet another type of improved variable reflectance mirror according to the invention, similar to that illustrated in Figure 4, the layer of laminating material is not present and electrode-bearing wall 100 is replaced with the prism-shaped piece of material on  
10 one surface of which is coated a layer of electrically conducting layer to serve as an electrode of the device of reversibly variable transmittance.

In the improved mirrors of the invention, the angle between the plane of the reflecting means or layer  
15 (e.g., layer 18A in Figure 3 and layer 20 in Figure 4) and the front surface (e.g., surface 101 in Figure 3 and surface 221 in Figure 4) is preferably about 1° to about 5°.

The laminating material, of layer 19 of  
20 mirror 300 of Figure 3 and layer 21 of mirror 400 of Figure 4, can be any transparent laminating material known in the art. Further, the process of laminating prism-shaped mirror 180 to surface 131 in mirror 300 or prism-shaped solid piece 22 to surface 101, is by any  
25 laminating process known in the art. In a preferred improved mirror of the invention, such as mirror 300, characterized by having the reflecting means be the reflecting means of a prism-shaped mirror, surface 131 will be of a piece of glass, solid material element 18  
30 of the prism-shaped mirror will be made of glass and the transparent laminating material will be polyvinyl butyral (PVB). Similarly, in a preferred improved mirror of the invention, such as mirror 400, characterized by having the reflecting means adhered  
35 directly to one surface of the device of reversibly variable transmittance and having a prism-shaped piece of solid-material laminated to the surface of the device

of reversibly variable transmittance, which is parallel to and spaced-apart from the surface to which the reflecting means is adhered, surface element 101 will be of a piece of glass, the prism-shaped piece of material  
5 will be made of glass, and the transparent laminating material will be PVB.

In Figures 3 and 4, wall 100, and elements 10 and 10A thereof; wall 130, and elements 13 and 13A thereof; spacer 11; solution space 12; and wire or  
10 strip 16 correspond to the same-numbered elements of device 200 illustrated in Figure 2. Wire or strip 15 in Figures 3 and 4 extends to a lead or extension which corresponds to lead 15A shown in FIGURE 2.

A mirror of the invention is usually mounted in  
15 a frame which shields from view all of the device of reversibly variable transmittance except most of the cross-sectional area (indicated by 14 in device 200 of Figure 2) of reversibly varied transmittance through which light reflected by the reflecting means of the  
20 mirror and seen by the observer of the mirror passes before and after reflecting from the reflecting means. The orientation of the frame can be manually or automatically adjustable. The leads 15A and 16A (illustrated in Figure 2) of the device will be  
25 connected to power supply control elements (e.g., switching means, means for controlling potential difference between the electrodes), which may optionally be located in the frame structure behind the device and the reflecting means or can be completely separate from  
30 the frame and mounting, and which, in turn, are connected to a power supply, such as a battery. Said power supply, particularly if small batteries, can also be located in the frame structure; usually, however, the power supply (e.g., an automobile battery) will be  
35 located outside the frame. The preferred application of the variable reflectance mirrors of the invention is as anti-glare rearview mirrors for automobiles.

When employed as the variable transmittance component of a variable transmittance light filter, particularly a window, a device of the invention will be framed essentially like a pane of glass in an ordinary window or windshield. All of the device, other than the portion thereof corresponding to most of the cross-sectional area (indicated by 14 in the device 200 of Figure 2), of reversibly varied transmittance, will be hidden from view by window frame components.

Similarly wires from leads, 15A and 16A of the device (illustrated in Figure 2) will be run inside such frame components, out of the view through the window, to power supply means and power supply control elements outside the window structure.

Display devices can be made with either or both of variable reflectance mirrors and variable reflectance light filters of the invention, wherein devices according to the invention are the variable transmittance components, and which, through variation in reflectance or transmittance, convey information. The area of the device of the invention that transmits or reflects light with variable intensity can be made to have the shape of desired symbols for a display device. Alternatively, separate devices of the invention can be arranged in suitable arrays to have the shape of desired symbols. In one embodiment, as the transmittance of the device or devices is decreased, the symbol represented becomes apparent to the viewer, as the device forms the dark symbol on a light background. In another embodiment, if the symbol is apparent at high transmittance of the device, because the symbol is surrounded by a dark background, activation of the device or devices will decrease transmittance and cause the symbol to fade from view. Virtually any symbol can be displayed with a display device employing a device of the invention as variable transmittance component, including letters, numerals, words, numbers or various

designs. Display devices employing the variable transmittance devices according to the invention are also useful in artistic displays, such as stained glass windows with panes of reversibly variable color.

5           The invention is illustrated in more detail in the following examples.

          Unless specified otherwise, all concentrations cited in the examples are at room temperature (20°-27°C) and all temperatures are in degrees Celsius.

10

#### EXAMPLE I

          A cell was formed by two sheets of glass 7.6 cm X 12.7 cm in area and separated by 0.020 cm thick strips of Nylon monofilament. The sheets of glass had  
15   been coated on one side with transparent conductive electrodes of indium-doped tin oxide (ITO), and these sides were placed so as to face each other on the inside of the cell. As illustrated in FIG. 2, the sheets were slightly offset from one another to provide two  
20   parallel, narrow, overhanging strips of ITO coating, along the 12.7 cm side of each of the sheets, on opposite sides of the volume for solution. Contacts were made by adhering, with conductive silver epoxy, copper strips along the narrow, overhanging strips of  
25   ITO coating and then the edges of the cell were sealed with insulating epoxy. Prior to final sealing, the space between the electrodes was filled with a propylene carbonate solution of 0.05 M N,N,N',N'-tetramethyl-1,4-phenylenediamine, 0.05 M 1,1'-diheptyl-4,4'-bipyridinium  
30   difluoroborate and 0.5 M tetra-n-butylammonium fluoroborate.

          When 1.0 volts was applied between the electrodes, the solution, which initially appeared colorless, changed to a deep blue-purple color. The  
35   solution returned to its bleached, colorless state when the cell was open-circuited or when the cell was short-circuited. The cell returned to its bleached

state more rapidly when the polarity of the 1.0 volt potential between the electrodes was reversed for several seconds and then the cell was short-circuited.

When the surface (opposite the ITO-coated surface) of one of the glass sheets was silvered, the device, when viewed through the unsilvered glass side, became a variable reflectance mirror.

#### EXAMPLE II

10 A cell that acted as a variable reflectance mirror was formed by two sheets of glass 10.2 cm X 10.2 cm in area and spaced by 0.013 cm thick beads of glass. One side of one of the glass sheets was coated with ITO and one side of the other sheet of glass  
15 was coated with a vacuum-deposited layer of Inconel metal. The cell was assembled with the ITO and Inconel electrode layers facing each other on the inside of the cell. The copper-strip contacts to the electrode surfaces, sealing and configuration of the device were  
20 the same as for the cell in Example I. The space between the electrodes was filled with a solution of 0.02 M 5,10-dihydro-5,10-dimethylphenazine, 0.02 M tetramethylene bis[4(1-benzylpyridine-4'-yl)-pyridinium]tetrafluoroborate, and 0.1 M tetra-n-  
25 butylammonium fluoroborate in propylene carbonate.

The reflectance from the Inconel electrode rapidly decreased when a potential of 1.0 volts was applied between the ITO and Inconel electrodes. The applied potential caused the solution layer to turn deep  
30 blue-green. Removal of the applied potential caused the solution to return to its clear, zero-potential equilibrium condition and the reflectance from the Inconel electrode to increase to the original high level, prior to application of the potential difference.



### EXAMPLE III

A device that acted as a variable transmittance light-filter or window was fabricated by spacing two sheets of glass, coated on one side with ITO, 0.013 cm apart, using glass beads for spacing. The dimensions of the sheets of glass were 6.4 cm X 25.4 cm. The ITO-coated sides of the sheets were facing. The copper-strip contacts, sealing and configuration of the device were the same as in the device of Example I, with the strips along the 25.4 cm sides of the sheets. The space between the electrodes was filled with a solution of 0.05 M 1,1'-dibenzyl-4,4'-bipyridinium difluoroborate and 0.05 M 5,10-dihydro-5,10-dimethylphenazine in propylene carbonate.

Application of a potential of 1.1 volts between the electrodes, across the solution layer, caused the white light transmittance of the device to decrease from 81.5% to 10.0% in 11 seconds. The steady-state transmittance of the device with 1.1 volts applied was 6.0%. The transmittance of the device, upon short-circuiting the electrodes, increased from 10% back to 70% in a period of 7 seconds and the transmittance increased back to 81.5% within 16 seconds after the electrodes were shorted. The device was cycled 40,000 times at room temperature between its transmittance at zero-applied potential and its steady-state transmittance with 1.1 volts applied between the electrodes. After the 40,000 cycles, the transmittance of the device at zero-applied potential was 78.5% and the steady-state transmittance at 1.1 volts applied potential remained at 6.0%. The speed of changes in transmittance was unchanged by the cycling.

When the device was cycled 20,000 additional times at 55°C, between transmittance at zero applied potential and steady-state transmittance at 1.1 volts, the transmittance at zero-applied potential decreased to 71.5% while that at 1.1 volts remained at 6.0%.

#### EXAMPLE IV

A device that acted as a variable transmittance light filter or window was fabricated like the device of Example III, except that the space between the electrodes was filled with a solution of 0.04 M 1,1'-di(n-heptyl)-4,4'-bipyridinium difluoroborate, 0.04 M 5,10-dihydro-5,10-dimethylphenazine and 0.1 M tetra-n-butylammonium fluoroborate in propylene carbonate.

Application of a potential of 1.1 volts between the electrodes, across the solution layer, caused the white light transmittance of the device to decrease from 84.5% to 20.0% in a period of 10 seconds. The steady-state transmittance of the device with 1.1 volts applied was 11.0%. The transmittance of the device, upon short-circuiting the electrodes, increased from 20% back to 70% in a period of 7 seconds and the transmittance increased back to 84.5% within 22 seconds after the electrodes were shorted. The device was cycled 40,000 times at room temperature between its transmittance at zero-applied potential and its steady-state transmittance with 1.1 volts applied between the electrodes. After the 40,000 cycles, the zero-applied potential transmittance was 84.0% and the transmittance at 1.1 volts applied potential was 11.0%. The speed of changes in transmittance was unchanged by the cycling.

When the device was cycled 20,000 additional times at 55°C, between transmittance at zero-applied potential and steady-state transmittance at 1.1 volts, the transmittance at zero-applied potential decreased to 77.5% while that at 1.1 volts remained at 11.0%.

#### EXAMPLE V

A device that acted as a variable transmittance light filter or window was fabricated like the device of Example III, except that the dimensions of the sheets of

ITO-coated glass were 6.4 cm X 7.6 cm. The solution between the electrodes was 0.05 M in 1,1'-dibenzyl-4,4'-bipyridinium difluoroborate and 0.05 M in 5,10-dihydro-5,10-dimethylphenazine in propylene carbonate.

Application of a potential of 1.1 volts between the electrodes, across the solution layer, caused the white light transmittance of the device to decrease from 81.5% to 10.0% in a period of 10 seconds. The steady-state transmittance of the device with 1.1 volts applied was 11.0%. The transmittance of the device, upon short-circuiting the electrodes, increased from 20% back to 70% in a period of 6 seconds and the transmittance increased back to 81.5% within 15 seconds after the electrodes were shorted. The device was cycled 40,000 times at 55°C between its transmittance at zero-applied potential and its steady-state transmittance with 1.1 volts applied between the electrodes. After the 40,000 cycles, the zero-applied potential transmittance was 65.0% and the steady-state transmittance at 1.1 volts applied potential remained at 6.0%. The speed of changes in transmittance was unchanged by the cycling.

#### EXAMPLE VI

A devices that acted as a variable transmittance light filter or window was fabricated like the device of Example III, except that the space between the electrodes was filled with a solution of 0.01 M N,N,N',N'-tetramethyl-1,4-phenylenediamine, 0.01 M 5,10-dihydro-5,10-dimethylphenazine, 0.01 M 1,1'-dibenzyl-4,4'-bypyridinium difluoroborate, 0.01 M tetramethylene bis[4(1-benzylpyridine-4'-yl)-pyridinium]tetrafluoroborate, and 0.1 M tetra-n-butyl ammonium fluoroborate in propylene carbonate.

Application of a potential of 1.2 volts between the electrodes, across the solution layer, caused the

white light transmittance of the device to decrease from 84% to 10% in a period of four seconds. Steady-state transmittance with 1.2 volts was 5%. Upon short circuiting of the electrodes, the transmittance of the  
5 device increased from 10% to 70% in a period of 6.5 seconds and increased back to the zero-potential equilibrium value of 84% within 15 seconds after the electrodes were shorted.

10

#### EXAMPLE VII

Devices, fabricated in essentially the same way as the device illustrated in Example III and filled with propylene carbonate solutions of the electrochromic compound combinations indicated below in Table VII, were  
15 found to operate as self-erasing, solution-phase electrochromic devices, similarly to those illustrated in Examples I to VI.

TABLE VII

	ANODIC ELECTROCHROMIC COMPOUND	CATHODIC ELECTROCHROMIC COMPOUND	
10			
15	1. 5,10-dihydro-5,10-dimethylphenazine	1,1'-di(n-heptyl)-4,4'-bipyridinium difluoroborate	
	2. 5,10-dihydro-5,10-dimethylphenazine	1,1'-di(n-heptyl)-4,4'-bipyridinium diperchlorate	
20	3. 5,10-dihydro-5,10-dimethylphenazine	1,1'-diphenyl-4,4'-bipyridinium difluoroborate	1
	4. 10-methylphenothiazine	1,1'-di(n-heptyl)-4,4'-bipyridinium difluoroborate	51
25	5. 10-ethylphenoxazine	1,1'-di(n-heptyl)-4,4'-bipyridinium difluoroborate	1
	6. tetrathiafulvalene	1,1'-dibenzyl-4,4'-bipyridinium difluoroborate	

### EXAMPLE VIII

Numerous compounds have been tested for acceptability as anodic or cathodic electrochromic compounds in the single-compartment, self-erasing, solution-phase devices of the invention, with propylene carbonate as solvent.

Some compounds were found to be unacceptable because of instability upon reduction (cathodic compounds) or oxidation (anodic compounds). Such instability is indicated by the absence of any, or the presence of only one, chemically reversible reduction wave (in the case of a cathodic compound) or chemically reversible oxidation wave (in the case of an anodic compound) in a voltammogram, obtained by any standard technique, of the compound in the solvent at room temperature.

No compound, which has at least two chemically reversible voltammetric reduction waves (if a cathodic compound) or at least two chemically reversible voltammetric oxidation waves (if an anodic compound) in a solvent, has been found to lead to unacceptable instability, particularly to cycling, when combined, in a solution in the solvent, with any other compound or compounds with the same property. This observation applies particularly to such combinations which include at least one cathodic compound and at least one anodic compound.

Clearly, to be acceptable, a compound must, upon reduction or oxidation in the solvent, undergo a change in extinction coefficient at at least one wavelength in the visible range ( $4200\text{\AA}$  to  $700\text{\AA}$ ). To insure stability, such a change must occur with the reduction corresponding to the first, or at least two, chemically reversible voltammetric reduction waves, if the compound is a cathodic compound, or the oxidation corresponding to the first, or at least two, chemically

reversible voltammographic oxidation waves, if the compound is an anodic compound.

Beyond being minimally acceptable as a cathodic or anodic electrochromic compound in a solution of the invention, a compound will desirably have a solubility, in its zero-potential equilibrium state in the solvent of such a solution, of at least about  $10^{-4}$  M at 25°C and will undergo, at at least one wavelength in the visible range, upon the reduction corresponding to the first chemically reversible voltammographic reduction wave, if a cathodic compound, or the oxidation corresponding to the first chemically reversible voltammographic oxidation wave, if an anodic compound, an increase in extinction coefficient by at least a factor of about  $10^2$  to at least about  $10^3 \text{ cm}^{-1} \text{ M}^{-1}$ .

Compounds that have been found to meet these criteria of acceptability and desirability, with propylene carbonate as solvent, are all of those specifically mentioned in any of Examples I to VII, and, in addition, the novel anodic compound, N,N',N''-trimethyltriphenazinoxazine, the known anodic compounds, o-tolidine, N,N,N',N''-tetramethylbenzidine, N,N,N',N''-tetraphenyl-1,4-phenylene diamine, and 5,10-dihydro-5,10-diphenylphenazine and the known cathodic compounds 1,1'-dimethyl-4,4'-bipyridinium dichloride, 1,1'-di(p-cyano phenyl)-4,4'-bipyridinium difluoroborate, and 1,1'-diphenyl-4,4'-bipyridinium diiodide.

30

#### EXAMPLE IX

This example illustrates that devices of the invention are useful as gray-scale devices, i.e., devices in which, by adjusting potential difference between the electrodes, transmittance can be adjusted to, and stabilized at, intermediate values between the "clear" (i.e., zero-potential equilibrium) value and the darkest

35

value that is possible to attain without impairing chemical stability.

A cell like that of Example III was constructed and filled with a solution which was 0.04 M in 1,1'-di(n-heptyl)-4,4'-bipyridinium difluoroborate and 0.04 M in 5,10-dihydro-5,10-dimethylphenazine in propylene carbonate. The steady-state transmittance of the cell to white light was measured as a function of the potential difference between the electrodes of the device, and the values indicated in Table IX were obtained.

TABLE IX

	Potential between the Electrodes (volts)	Steady-State Transmittance (%)
15	0.0	83
	0.1	83
	0.2	83
	0.3	83
20	0.4	81.5
	0.5	71.5
	0.6	56.0
	0.7	42.0
	0.8	31.0
	0.9	24.0
	1.0	17.0
25	1.1	13.0
	1.2	11.5

EXAMPLE X

A device that acted as a variable reflectance mirror with a thickened solution was fabricated by coating the ITO surface of an ITO-coated piece of glass with a dichloroethane solution of the acrylic sheet material, LUCITE L. Upon evaporation of the dichloroethane, a thin film of acrylic sheet material weighing 0.29 grams was left on the ITO surface. This same piece of glass had a conventional-mirror, silvered coating on the side opposite the ITO-acrylic material side and was used to prepare a cell by spacing the



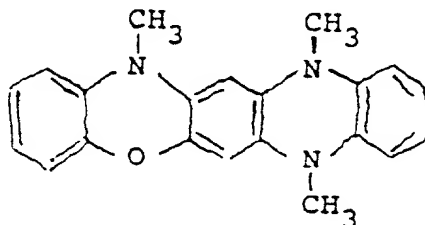
ITO-acrylic side 0.013 cm from the ITO side of a second piece of glass which had only an ITO coating on one side. Spacing was with glass beads. The dimensions of the sheets of glass were 6.4 cm X 25.4 cm. The  
5 copper-strip contacts, sealing and configuration of the device were the same as that in Example III. The space between the ITO-acrylic side of the one piece of glass and the ITO side of the other piece of glass was filled with a solution of 0.04 M 1,1'-di-n-heptyl-4,4'-bipyridinium difluoroborate, 0.04 M 5,10-dihydro-5,10-dimethyl  
10 phenazine and 0.1 M tetrabutylammonium fluoroborate in propylene carbonate.

Within several hours at room temperature, the acrylic layer had dissolved in the propylene carbonate  
20 solution, resulting in thickening, and the device could be operated as a variable reflectance mirror by varying the potential across the solution between the ITO electrode layers. With an applied voltage of 1.2 volts, the reflectance changed from 73.5% to 20.0% in a period  
25 of 2.5 seconds and reached a steady state reflectance of 9.0%. Upon short circuiting the electrodes, the reflectance increased from 9.0% to 60.0% in a period of 17 seconds and eventually increased back to the clear, zero-potential value of 73.5%.

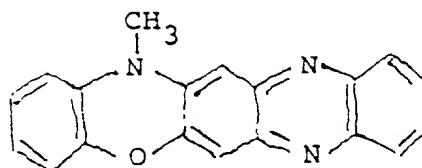
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#### EXAMPLE XI

Synthesis of N,N',N''-trimethyltriphenazinoxazine



The compound was made, starting with the known compound, N-methyltriphenazinoxazine, of Formula



by following the procedure described by Gilman and Dietrich, J. Amer. Chem. Soc. 79, 6178 (1957), for  
10 converting phenazine to  
5,10-dihydro-5,10-dimethylphenazine. 100 milligrams of the starting compound (0.33 mmoles), 25 milligrams of potassium metal (0.67 mmoles) and 5 ml of ethylene glycol dimethyl ether were stirred for 12 hours. Then  
15 an excess of methyl iodide was added, followed by absolute ethanol to destroy excess potassium.

The reaction mixture was then mixed with water. The resulting precipitate was recrystallized from ethanol to yield approximately 2 milligrams of pure  
20 product.

In propylene carbonate, the product was found to have chemically reversible oxidation waves and color changes very similar to those of 5,10-dihydro-5,10-dimethylphenazine.

25

#### EXAMPLE XII

A device with the configuration illustrated in FIG. 3 was fabricated by laminating, using a standard procedure with the clear laminating material  
30 polyvinylbutyral (PVB), an electrochromic device like that in Example III to a conventional, prism-shaped, automobile rearview mirror. The device was filled with a solution of 0.02 M 1,1'-dibenzyl-4,4'-bipyridinium difluoroborate, 0.02 M 5,10-dihydro-5,10-dimethylphenazine,  
35 and 0.1 M tetra-n-butylammonium fluoroborate in propylene carbonate. This device was used as the rearview mirror inside an automobile. During operation,

the device provided a distortion-free, continuously variable reflectance (i.e., gray-scale) mirror which was extremely effective in eliminating glare due to headlights on vehicles approaching from behind during  
5 night driving.

The device was operated at zero-potential difference when there was little or no glare from headlights of vehicles approaching from behind, 0.6 volts potential difference when there was moderate  
10 glare, and 1.0 volts when there was high glare.

The clear state reflectance from the silvered surface of the prism mirror at zero applied potential was greater than 70% of the light incident on the device. The steady state reflectance from the silvered  
15 surface at 0.6 volts applied potential was about 30% and at 1.0 volts applied potential the reflectance was about 10%.

Although the invention has been described with some specificity, those of skill will recognize numerous variations and modifications of the specifics that are  
20 within the spirit of the invention. The variations and modifications are also within the scope of the invention as disclosed and claimed herein.

WHAT IS CLAIMED IS:

1. A solution, for use as the variable transmittance medium in a single-compartment, self-erasing, solution-phase electrochromic device, which comprises:
  - (A) a solvent;
  - (B) at least one cathodic electrochromic compound which, in a voltammogram done in the solvent at room temperature, displays at least two chemically reversible reduction waves, with the first of said reductions accompanied by an increase in molar extinction coefficient at at least one wavelength in the visible range;
  - (C) at least one anodic electrochromic compound which, in a voltammogram done in the solvent at room temperature, displays at least two chemically reversible oxidation waves, with the first of said oxidations accompanied by an increase in molar extinction coefficient at at least one wavelength in the visible range; and
  - (D) if all cathodic and anodic compounds in their zero-potential equilibrium states in the solution are not ionic, an inert current-carrying electrolyte.
2. An electrochromic device, comprising a single compartment, self-erasing, solution-phase variable transmittance component that provides continuously variable transmittance over a range of transmittance as a function of the potential difference applied, and wherein the sheet resistance of a transparent electrode layer of the electrochromic device is less than 40 ohms per square.
3. An electrochromic device, comprising a single compartment, self-erasing, solution-phase, variable transmittance component, where said electrochromic device is gray-scale controllable over a range of transmittance by applying potential differences between electrode layers of the device of 0.2 to 1.4 volts.
4. An electrochromic device, comprising a single compartment, self-erasing, solution-phase variable transmittance component, where said electrochromic device provides a range of white light transmittance from greater than about 81% to about 10% or less.
5. An electrochromic device, comprising a single compartment, self-erasing, solution-phase, variable transmittance component, where said electrochromic

device provides continuously variable transmittance over a range of transmittance as a function of the potential difference applied, and wherein the electrochromic device provides a light transmittance as low as about 10% or less.

6. An electrochromic device, comprising a self-erasing variable transmittance component, where said electrochromic device provides continuously variable transmittance over a range of transmittance as a function of the potential difference applied, and wherein the sheet resistance of a transparent electrode layer of the electrochromic device is less than 40 ohms per square.

7. An electrochromic device, comprising a self-erasing variable transmittance component, where said electrochromic device is gray-scale controllable over a range of transmittance by applying potential differences between the electrode layers of the device of 0.2 to 1.4 volts.

8. An electrochromic device, comprising a self-erasing variable transmittance component, where said electrochromic device provides a range of white light transmittance from greater than about 81% to about 10% or less.

9. An electrochromic device according to any of claims 2-8, wherein said device is an electrochromic window that has an area of at least about 162 square centimeters.

10. An electrochromic device according to any of claims 2-8, wherein said transmittance is reduced from greater than about 80% to less than 10% with a potential difference of less than 1.2 volts.

ABSTRACT

SINGLE-COMPARTMENT, SELF-ERASING,  
SOLUTION-PHASE ELECTROCHROMIC DEVICES,  
SOLUTIONS FOR USE THEREIN, AND USES THEREOF

5           Single-compartment, self-erasing,  
solution-phase electrochromic devices, solutions of  
electrochromic compounds for use as media of variable  
transmittance in such devices, and electrochromic  
compounds for such solutions are provided. The devices  
10 of the invention are surprisingly stable to cycling  
between light and dark states, have continuously  
variable transmittance to light as a function of  
electrical potential applied across the solution in a  
device, and have transmittance that can be varied over  
15 more than a factor of 10, from clear to dark or from  
dark to clear, in several seconds. Thus, the devices  
are especially suitable as variable transmittance  
components of variable transmission light filters,  
including windows, and variable reflectance mirrors,  
20 including anti-glare rearview mirrors in automobiles.  
Also provided are improved variable reflectance mirrors,  
wherein transmittance of reflected light is varied by  
thermochromic, photochromic or electro-optic means and  
wherein the reduction in transmittance which is required  
25 to eliminate perceptible reflection of an object to the  
eyes of an observer is reduced by disposing the plane of  
the highly reflective surface of the mirror at an angle  
with respect to the plane of the surface through which  
light from the object enters the mirror.



FIG. 3

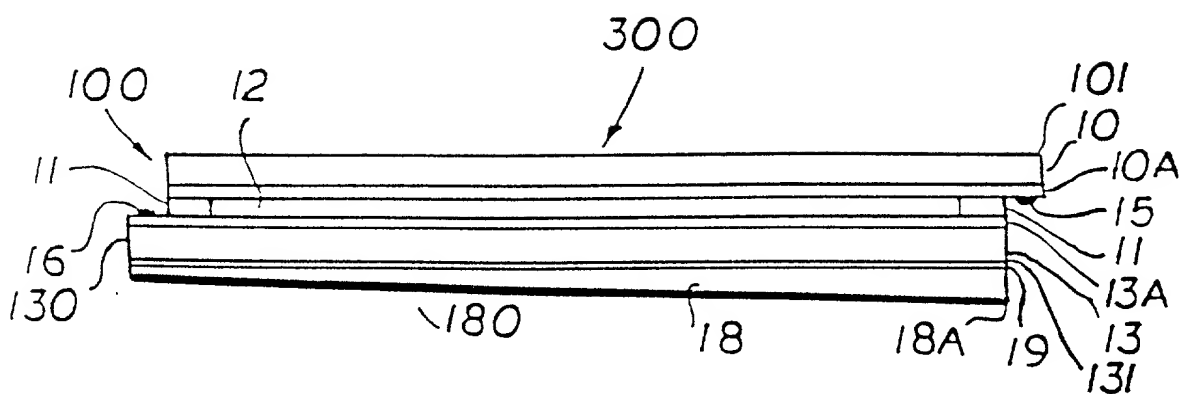
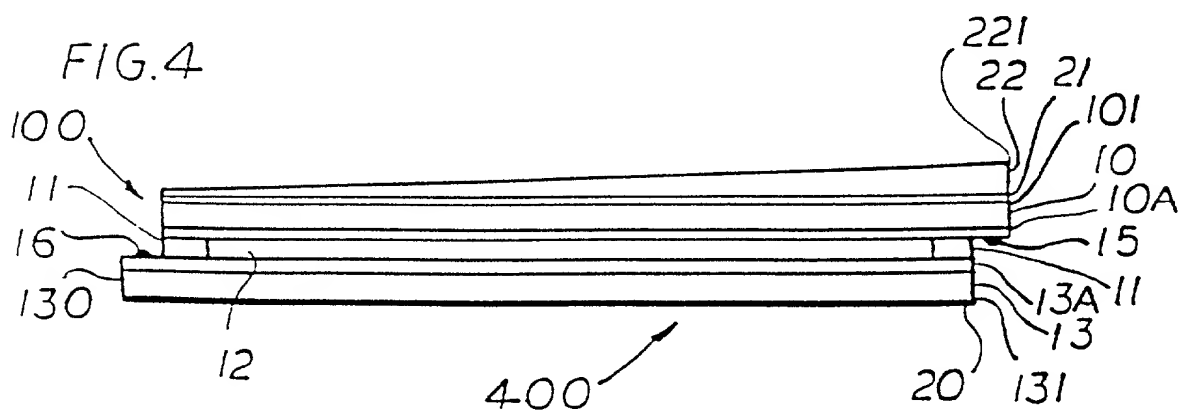


FIG. 4





DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled SINGLE-COMPARTMENT, SELF-ERASING, SOLUTION-PHASE ELECTROCHROMIC DEVICES, SOLUTIONS FOR USE THEREIN, AND USES THEREOF the specification of which (check one)

- (x) is attached hereto.  
 ( ) was filed by an authorized person on my behalf on \_\_\_\_\_ as Application Serial No. \_\_\_\_\_ and was amended on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and so identified, and I have also identified below any foreign application for patent or inventor's certificate on this invention filed by me or my legal representatives or assigns and having a filing date before that of the application on which priority is claimed.

<u>Number</u>	<u>Country</u>	<u>Day/Month/Year Filed</u>	<u>Priority Claimed (Yes or No)</u>
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N/A

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

<u>Application Serial No.</u>	<u>Filing Date</u>	<u>Status</u>
-------------------------------	--------------------	---------------

N/A

hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

I hereby appoint the following attorneys, with full power of substitution and revocation, to prosecute this application and to transact all business in the United States Patent and Trademark Office connected therewith and request that all correspondence and telephone calls in respect to this application be directed to FITCH, EVEN, TABIN & FLANNERY, Suite 900, 135 South LaSalle Street, Chicago, Illinois 60603, Telephone No. (312) 372-7842:

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On: February 5, 1997

By:   
William J. Scanlon

PATENT APPLICATION

Attorney Docket No.: 55748/140

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: H. Byker  
Serial No.: 08/175,781  
Filed: December 30, 1993  
For: VARIABLE REFLECTANCE AUTOMOBILE MIRROR

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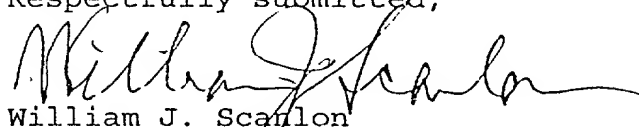
Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

The undersigned, having power of attorney in the above-specified Application, hereby appoints as an additional attorney to prosecute the Application and to transact all business in the Patent and Trademark Office connected therewith and with the resulting Patent:

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